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# STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION. PART XXI. THE ROTATORY DISPERSION OF STEREOISOMERIC HYDROXYPHENYLAMINOMETHYLENECAMPHORS AND THEIR ACETYLATED AND BENZOYLATED DERIVATIVES

By Bawa Kartar Singh and Sailesh Chandra Sen

Aminophenols (*o*-, *m*- & *p*-) have been condensed with oxymethylenecamphors (*d*, *l* & *dl*). The rotatory power of the optically active isomerides (*d* and *l*) is found to be identical and can be expressed by the simple dispersion equation of Drude, $[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}$.

The replacement of a hydrogen atom by a negative group such as hydroxyl diminishes the rotation. The effect of substitution on optical activity is represented by a series which agrees, subject to minor variations, with the *polar* one. The acetylation of the hydroxyl group reduces the rotation of the parent compound. The fall in rotatory power is remarkably great on benzoylation. The influence of solvent as well as that of position isomerism on optical rotatory power is also discussed.

In this communication we present further experimental data on the rotatory dispersion of the condensation products of oxymethylenecamphors (*d*,*l* and *dl*) with aminophenols (*o*-, *m*- and *p*-) and their acetylated and benzoylated derivatives.

The condensation products of oxymethylenecamphors (*d*, *l*, and *dl*) with *p*-aminophenol are difficult to crystallise.

*The Influence of Chemical Constitution on the Character of Rotatory Dispersion.*—According to the electrostatic modification of Thomson's rule (*Phil. Mag.*, 1923, **46**, 497) as suggested by Rule (*J. Chem. Soc.*, 1924, **125**, 1121), there is a close relation between the optical rotation of a compound and the electrochemical nature of the substituent groups. The introduction of an electronegative group such as hydroxyl would result in a decrease of the optical rotation of the parent compound. This is corroborated by our experimental results (Table A).

On a careful study of the rotatory power data for the substituted anilinomethylenecamphors (*o*-, *m*- and *p*-) in different solvents given in Table A, we find that among the position isomerides the influence of substituents on rotatory power is as follows :

For the *ortho* compounds, $H > OH > Cl > Br$ in all solvents.
For the *meta* compounds, $H > CH_3 > OH > Cl > Br > I$ in 3 solvents ;
and $H > OH > CH_3 > Cl > Br > I$ in 2 solvents.
For the *para* compounds, $H > OH > CH_3 > Cl > Br > I$ in 4 solvents.

The position of the hydroxyl group (OH) in the polar series is not known with certainty.

The specific inductive capacity on non-polar compounds of the type $C_6H_5X$ arranges in the following sequence :—$NO_2 > CN > COMe > CHO > Cl > OH > NH_2 > Br > N(Me)_2 > OMe > Et > H$ (Landolt), although for phenol it is not strictly comparable as it has been determined at 48° and not at the ordinary temperature as

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with other compounds. The dissociation constant of substituted benzoic acids arranges in the order :—$NO_2 > COOH > Br > Cl > OH > Me > OMe > H > NH_2 > NMe_2$ (Landolt). This agrees well with the series obtained experimentally from optical rotation subject to minor variations as stated above ; the position of Me and OH groups often inrerchanging between themselves.

*The Influence of Substituents on Rotatory Power of the Position Isomerides.*—The sequence of rotatory power of the position isomerides of the hydroxy compound (Table A) is un>*p*>*o*>*m* in methyl alcohol, ethyl alcohol, acetone and pyridine, but un>*p*>*m*>*o* in chloroform. In the case of the acetoxy derivatives, the sequence of decreasing rotatory power in ethyl alcohol is un>*o*>*p*>*m*. This is, however, neither in agreement with Frankland's lever arm hypothesis (*J. Chem. Soc.*, 1896, **69**, 1583) nor with the electrostatic modification as suggested by Rule (*loc. cit.*), as the unsubstituted compound has always the highest rotatory power in all these cases. This point has already been emphasised in previous communications (Singh, Mallick and Bhaduri, *J. Indian Chem. Soc.*, 1931, 8, 95 ; Singh, Bhaduri and Barat, *loc. cit.* Singh and Bhaduri, *Proc. Ind. Acad. Sci.*, 1942, A, **15**, 283).

In the above discussion the comparison is confined to the green mercury line (A. U. 5461), but if it is made for the red lithium line (A. U. 6708), the order of position isomerides is changed ; for example in methyl alcohol, it is un>*p*>*m*>*o* ; the *o*- and *m*- isomerides interchanging In order to overcome this difficulty in compounds which show simple dispersion, *i.e.* obey the one-term Drude equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$, the values of $K_0$ (the absolute rotation) may be compared. These values are for $\lambda$ (where $\lambda^2 - \lambda^2_0 = 1$) always in the infra-red region beyond 10,000 A. U. and are independent of the wave-length. The values of $K_0$, given in the tables (I to VI & A) do not also support the above mentioned rules regarding the order of rotatory power of the position isomerides.

*Effect of Acetylation and Benxoylation.*—Rule (*loc. cit.*) anticipated that the substitution of a hydroxylic hydrogen atom by a negative alkyl or a positive benzoyl group would influence the rotation in opposite direction. Frankland and Carter (*J. Chem. Soc.*, 1912, **101**, 2470) have shown that the introduction of the benzoyl group alters the rotation of amyl alcohol from −3·87° to +9·52° and it is thus equivalent to an increase in positive rotation. But Singh and Bhaduri (*J. Indian Chem. Soc.*, 1930, 7, 550) have, however, shown that the acetyl derivative of *p*-phenylenebisamino-*d*-camphor has much lower rotation than the parent compound. Our present experiments also show that the rotatory power of the acetoxy derivatives of anilinomethylenecamphors is lower than that of the parent hydroxy derivatives (*vide* Tables I—VI).

The benzoyl derivative has still a remarkably lower rotation (Table VII). These facts are against Thomson's generalisation and may be illustrated from the values of $[\alpha]^{35°}_{5461}$ in ethyl alcohol :—

| | |
|---|---|
| *p*-Hydroxyphenylaminomethylenecamphor, | 450·5° |
| *p*-Acetoxyphenylaminomethylenecamphor, | 190·3° |
| *p*-Benzoxyphenylaminomethylenecamphor, | 6·2° |

*The Effect of the Nature of Solvent on Rotatory Power.*—The specific rotatory power for Hg $_{green}$ line of the compounds in different solvents is given in Table A. It is found that the order of increasing rotatory power is methyl alcohol>ethyl alcohol>acetone>pyridine and chloroform. The positions of chloroform and pyridine are, however, frequently interchanging which is approximately in the order of the dielectric constant of the solvents.

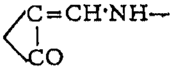
TABLE A.

$[\alpha]^{35^\circ}_{Hg_{green}}$ for the *dextro* isomerides.

| Formula of the substance | MeOH. | EtOH. | $Me_2CO$. | Pyridine. | $CHCl_3$. |
|---|---|---|---|---|---|
| * R. $C_6H_5$ ... ... | 480·0°<br>(86·8) | 451·3°<br>(83·1) | 448·9°<br>(81·2) | 433·2°<br>(81·2) | 424·6°<br>(78·6) |
| * R. $C_6H_4$. Me (*m*-) ... | 454·4<br>(85·2) | 439·9<br>(81·0) | 442·3<br>(82·3) | 405·8<br>(80·5) | 384·8<br>(68 6) |
| * R. $C_6H_4$. Me (*p*-) ... | 465·0<br>(79·6) | 440 8<br>(80 1) | 425·8<br>(78 8) | 401·6<br>(74·1) | 401·6<br>(74·1) |
| ** R. $C_6H_4$ Cl (*o*-) ... | 400·2<br>(64·8) | 405·8<br>(72·2) | 380 0<br>(61·4) | 391·3<br>(63·7) | 386·0<br>(61·8) |
| ** „ (*m*-) | 388·5<br>(63·1) | 384·7<br>(62·5) | 388·0<br>(63·7) | 374·4<br>(63·7) | 381·4<br>(61·2) |
| ** „ (*p*-) ... | 417·7<br>(75·3) | 406·3<br>(73 2) | 401·8<br>(70·6) | 394·4<br>(68·2) | 374·6<br>(67·6) |
| ** R. $C_6H_4$ Br (*o*-) ... | 347·5<br>(53·7) | 339·9<br>(55·1) | 330·1<br>(54·1) | 328·4<br>(51·9) | 329·0<br>(51·8) |
| ** „ (*m*-) ... | ... | 354·0<br>(63·5) | 348·4<br>(64·7) | 334·3<br>(59 2) | 324·1<br>(56·7) |
| ** „ (*p*-) ... | 361·1<br>(63 7) | 355·6<br>(62 4) | 360·6<br>(65·3) | 348·8<br>(53 6) | 324·3<br>(57·3) |
| ** R. $C_6H_4$ I (*m*-) ... | 328·5<br>(60·4) | 319·5<br>(58·5) | 309·7<br>(57·6) | 294·8<br>(53·6) | 279·1<br>(51·1) |
| ** „ (*p*-) ... | 338 1<br>(59·0) | 325·9<br>(54 3) | 326 5<br>(55·2) | 318 4<br>(54·9) | 300 9<br>(54·5) |
| R. $C_6H_4$ ·OH (*o*-) ... | 437·5<br>(75·1) | 436·2<br>(74·6) | 419·6<br>(79 0) | 413 3<br>(68·5) | 409·8<br>(66·5) |
| „ (*m*-) ... | 435·4<br>(78·5) | 417·1<br>(82 8) | 412·6<br>(79·5) | 410·5<br>(80·1) | 389·5<br>(770) |
| „ (*p*-) ... | 456·5<br>(83·1) | 450·5<br>(80·8) | 430·0<br>(74·7) | 426 2<br>(73·5) | 418·0<br>(76·5) |
| R. $C_6H_4$ O· OC. Me (*o*-) | ...<br>... | 264·8<br>(53·3) | 254·3<br>... | ...<br>... | 266·3<br>(47 2) |
| „ (*m*-) | 189·1<br>(42·2) | 181·1<br>(40·4) | 180 9<br>(32·2) | ...<br>... | ...<br>... |
| „ (*p*-) | 202·2<br>(39·2) | 190·3<br>(38·6) | ...<br>... | 180·9<br>(41·8) | ...<br>... |

* Singh, Bhaduri and Barat, *J. Indian Chem. Soc.*, 1931, 8, 345.

** Singh and Bhaduri, *Proc. Ind. Acad. Sci.*, 1937, A, 6, 341; 1939, 10, 359. R = $C_8H_{14}$



$$C_8H_{14}\left\langle\begin{array}{l} C{=}CH{\cdot}NH{-} \\ \,| \\ CO \end{array}\right.$$

(*a*) Figures within brackets refer to the numerical value of *Ko* of the Drude equation, $[\alpha] = \frac{Ko}{\lambda^2-\lambda_0^2}$, referred to on p. 3 for $\lambda_r$ when $\lambda = \sqrt{\lambda_0^2+1}$.

The rotatory dispersion of these compounds is found, as with other compounds of the series (Singh and Badhuri, *J. Indian Chem. Soc*, 1930, **7**, 771; 1931, **8**, 181, 625, 623; Singh, Bhaduri and Barat, *ibid.*, 1931, **8**, 345) to obey the simple dispersion equation of Drude, $[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}$ But *p*-benzoxyphenylaminomethylenecamphor does not, however, obey this one term formula : the plot of $1/\alpha$ against $\lambda^2$ is not a straight line, but a steep curve. It, therefore, exhibits *complex* dispersion.

*The Physical Identity of Enantiomers.*—According to Pasteur's principle of molecular dissymmetry, the *d*-and *l*-forms are represented as true mirror images of one another differing in sign but absolutely identical in the numerical value of the rotatory power. The numerical values of the rotatory power of the two forms (Table I—VI) are identical within the limit of experimental errors. Out of 200 observations now recorded, in as many as 125 cases, the difference in the numerical values of specific rotatory power of the opposite isomers corresponds to a difference of less than 0·01° in the observed angle of rotation and in 72 other cases the corresponding angle lies between 0·01° and 0·02°, which is the limit of experimental error allowable in such measurements. Only in the remaining cases, *viz.* *m*-hydroxyphenylaminomethylenecamphor in pyridine for $Ag_{5209}$ (Table II) and *p*-acetoxyphenylaminomethylenecamphor in pyridine for $Hg_{5460}$ (Table VI), the difference corresponds to between 0·02° and 0·03° in the observed angle of rotation. These, however, are of the nature of casual experimental errors.

Whether a racemic form is a *dl*-compound of the *d*-and *l*-isomers can be sometimes inferred from the melting point determinations*. Three cases arise : (*a*) The melting point of the racemic form is higher than that of the active forms, in which case it is a true *dl*-compound at least in the solid state. The racemic form of *o*-acetoxyphenylaminomethylenecamphor is an instance of this nature. (*b*) The melting point of the racemic form is lower than that of the active forms, as in the case of *o*-hydroxy- and *p*-hydroxyphenylaminomethylenecamphors. In this case for the characterisation of the racemic modification, the preparation of its freezing point-composition curve with the corresponding *d*- or *l*-form will be necessary. (*c*) The melting point of the racemic form is identical with that of the active forms as in the case of *m*-hydroxy- and *m*-acetoxyphenylaminomethylenecamphors. Some more examples of the racemic form having identical melting points with those of the active forms have been already cited (Singh and Bhaduri, *J. Indian Chem. Soc.*, 1931, **8**, 623; *Proc. Ind. Acad. Sci.*, 1942, A, **15**, 282). In this case, as in the first, the racemic modification is a *dl*- compound.

## EXPERIMENTAL

*Preparation of* o-, m-*and* p-*Hydroxyphenylaminomethylene*-d-*camphor.*—Oxymethylene-*d*-camphor (1 mol.) in methyl alcoholic solution was added to the acetic acid solution of *o*-, *m*- or *p*-aminophenol (1 mol.) and kept for ½ hour. The mixture was then poured into water and the colourless product obtained was crystallised from dilute alcohol. The condensation products of oxymethylenecamphors (*d*-, *l*- and *dl*-) with *p*-aminophenol were difficult and slow to crystallise. On keeping the dilute alcoholic solution of the crude products for 10 to 15 days, they were obtained as rectangular blocks.

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* This will not characterise a racemic solid solution.

Acetyl derivatives of the above compounds were prepared by warming the hydroxy compounds with acetyl chloride on the water-bath for about hour. The reaction mixture was poured into water ; an oil separated which solidified on stirring with sodium carbonate. The solid mass, thus obtained, was crystallised from dilute alcohol. The laevo and racemic forms were prepared in the same way.

The melting points, time of crystallisation and analytical data are tabulated below.

### TABLE B.

*Hydroxy- and acetoxy-phenylaminomethylenecamphors.*

| | | Hydroxy compounds. | | | | | | | Acetoxy compounds. Colourless needles. Time of crystallisation, 15—20 days. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | M.p. | Appearance. | Time of crystallisation. | Analysis (found %) | | | | | M.p. | Analysis (found %) | | |
| | | | | | C. | H. | N. | | | | C. | H. | N. |
| *ortho-* | *d* | 180-182° | Colourless needles. | 3-4 hours | 75·1 | 7·75 | — | *ortho-* | *d* | 131-32° | 72·6 | 8·0 | — |
| | *l* | ,, | ,, | ,, | 75·2 | 7·87 | — | | *l* | ,, | — | — | 4·54 |
| | *r* | 164-65 | ,, | ,, | 75·1 | 7·80 | — | | *r* | 140-42 | — | — | 4·58 |
| *meta-* | *d* | 165 | ,, | 3-4 days | 75·1 | 7·55 | 5·16 | *meta-* | *d* | 140-42 | — | — | 4·54 |
| | *l* | ,, | ,, | ,, | 75·1 | 7·7 | 5·4 | | *l* | ,, | 72·99 | 7·6 | — |
| | *r* | ,, | ,, | ,, | — | — | 5·49 | | | | | | |
| *para-* | *d* | 158-60 | Yellowish rectangles | 15-20 days | 74·7 | 7·72 | — | *para-* | *d* | 220-22 | 73·1 | 7·5 | 4·52 |
| | *l* | ,, | ,, | ,, | 75·5 | 7·9 | — | | *l* | ,, | 72·99 | 7·6 | — |
| | *r* | 150-52 | ,, | ,, | — | — | 5·57 | | *r* | 195-97 | — | — | 4·70 |
| | | | $C_{17}H_{21}O_2N$ requires | | 75·27 | 7·74 | 5·43 | | | $C_{19}H_{23}O_3N$ requires | 73·18 | 7·35 | 4·47 |

*p-Benzoxyphenylaminomethylene-d-camphor* was prepared by shaking the *p*-hydroxy compound with benzoyl chloride and excess of sodium hydroxide for 2 hours. The oily substance, thus obtained, was crystallised from dilute alcohol as colourless needles, m. p. 236-37°. (Found : N, 3·73. $C_{24}H_{25}O_3N$ requires N, 3·82 per cent).

The compound is soluble in methyl and ethyl alcohol, ether, chloroform, acetone and sparingly so in benzene.

The benzoyl derivatives of *o*- and *m*-hydroxy compounds are oils which refused to solidify.

The rotatory power determinations were made in a 2-d cm. jacketted tube at 35°. The value of $\lambda_0$, calculated from the dispersion formula, is given in the following tables and is expressed as $\mu$ or $10^{-4}$ cm.

TABLE I.

*o-Hydroxyphenylaminomethylenecamphors.*

| Solvent: | | Ethyl alcohol. | | Methyl alcohol. | | Acetone. | | Pyridine. | | Chloroform. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. (g./100 c.c.) | *d* | 0·4024 | | 0·4000 | | 0·4028 | | 0·3992 | | 0·3672 | |
| | *l* | 0·4000 | | 0·4016 | | 0·4028 | | 0·4020 | | 0·4012 | |
| Calculated | [α] | $\pm\frac{74·65}{\lambda^2-0·1270}$ | | $\pm\frac{75·10}{\lambda^2-0·1261}$ | | $\pm\frac{79·05}{\lambda^2-0·1048}$ | | $\pm\frac{68·53}{\lambda^2-0·1320}$ | | $\pm\frac{66·51}{\lambda^2-0·1399}$ | |
| | $\lambda_0$ | 0·3564 | | 0·3552 | | 0·3238 | | 0·3634 | | 0·3741 | |
| Line. | | Obs. [α] | | Obs. [α] | | Obs. [α] | | Obs. [α] | | Obs. [α] | |
| | | *d* | *l* | *d* | *l* | *d* | *l* | *d* | *l* | *d* | *l* |
| $Cd_{5086}$ | | +566·8° | −567·5° | +566·3° | −565·4° | +514·0° | −516·5° | +542·6° | −541·2° | +561·0° | −560·9° |
| $Ag_{5209}$ | | 517·0 | 517·5 | 517·3 | 515·5 | 475·5 | 474·3 | 492·9 | 491·3 | 506·4 | 506·0 |
| $Hg_{5460}$ | | 436·2 | 436·2 | 437·5 | 436·9 | 409·8 | 408·5 | 413·3 | 411·8 | 419·6 | 420·1 |
| $Hg_{5780}$ | | 360·4 | 360·1 | 362·5 | 361·1 | 343·9 | 345·1 | 339·5 | 339·8 | 343·1 | 342·8 |
| $Na_{5892}$ | | 339·2 | 338·8 | 338·8 | 339·9 | 327·8 | 326·6 | 317·3 | 318·7 | 320·1 | 320·4 |
| $Li_{6103}$ | | 304·5 | 304·3 | 305·0 | 305·1 | 295·5 | 295·5 | 279·0 | 278·7 | 285·9 | 286·6 |
| $Cd_{6438}$ | | 259·7 | 258·8 | 260·0 | 259·0 | 254·6 | 255·8 | 243·0 | 242·6 | 242·4 | 243·1 |
| $Li_{6708}$ | | 231·1 | 231·3 | 231·3 | 231·6 | 229·7 | 228·5 | 215·3 | 216·4 | 213·9 | 214·4 |
| | | No mutarotation. | | No mutarotation | | No mutarotation | | No mutarotation | | No mutarotation | |

## TABLE II.

*m-Hydroxyphenylaminomethylenecamphors.*

| Solvent: | | Ethyl alcohol. | | Methyl alcohol. | | Acetone. | | Pyridine. | | Chloroform. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. (g /100 c.c.) | d | 0·4004 | | 0·4008 | | 4·4000 | | 0·3812 | | 0·4032 | |
| | l | 0·4004 | | 0·4008 | | 0·4004 | | 0·4012 | | 0·4016 | |
| Calc. | [α] | $\pm\frac{82{\cdot}80}{\lambda^2-0{\cdot}0991}$ | | $\pm\frac{78{\cdot}53}{\lambda^2-0{\cdot}1183}$ | | $\pm\frac{79{\cdot}50}{\lambda^2-0{\cdot}1028}$ | | $\pm\frac{80{\cdot}11}{\lambda^2-0{\cdot}1029}$ | | $\pm\frac{77{\cdot}00}{\lambda^2-0{\cdot}0998}$ | |
| | $\lambda_0$ | 0·3149 | | 0·3440 | | 0·3207 | | 0·3209 | | 0·3160 | |
| Line. ... ... | | Obs. [α] | | Obs. [α] | | Obs. [α] | | Obs, [α] | | Obs. [α] | |
| | | d | l | d | l | d | l | d | l | d | l |
| $Cd_{5086}$ ... ... | | +519·5° | −518·5° | +557·6° | −557·6° | +516·3° | −515·5° | +514·2° | −514·4° | +482·6° | −482·1° |
| $Ag_{5209}$ ... ... | | 480·2 | 481·2 | 514·0 | 512·7 | 478·8 | 478·1 | 473·4 | 477·4 | 447·8 | 447·0 |
| $Hg_{5460}$ ... ... | | 417·1 | 415·9 | 435·4 | 435·4 | 412·6 | 410·9 | 410·5 | 409·0 | 389·5 | 388·5 |
| $Hg_{5780}$ ... ... | | 354·7 | 352·2 | 363·1 | 364·3 | 347·5 | 348·8 | 347·5 | 346·6 | 328·7 | 328·0 |
| $Na_{5893}$ ... ... | | 333·6 | 335·5 | 341·7 | 342·0 | 330·0 | 329·9 | 327·8 | 327·9 | 311·4 | 312·9 |
| $Li_{6103}$ ... ... | | 303·5 | 304·0 | 307·0 | 308·2 | 298·8 | 298·8 | 295·2 | 295·3 | 281·6 | 281·4 |
| $Cd_{6438}$ ... ... | | 262·4 | 262·5 | 266·6 | 264·5 | 257·6 | 257·8 | 257·1 | 258·0 | 245·7 | 245·3 |
| $Li_{6708}$ ... ... | | 236·1 | 235·7 | 236·2 | 238·2 | 231·3 | 231·6 | 231·2 | 230·7 | 219·6 | 220·4 |
| | | | | | | | | No mutarotation | | No mutarotation | |

## TABLE III.

*p-Hydroxyphenylaminomethylenecamphors.*

| Solvent: | | Ethyl alcohol. | | Methyl alcohol. | | Acetone | | Pyridine. | | Chloroform. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. (g./100 c. c.) | d | 0·4000 | | 0·4020 | | 0·3984 | | 0·4000 | | 0·4008 | |
| | l | 0·4000 | | 0·4004 | | 0·3992 | | 0·4008 | | 0·4000 | |
| Calc. | [α] | $\pm\frac{80·85}{\lambda^2-0·1195}$ | | $\pm\frac{83·10}{\lambda^2-0·1164}$ | | $\pm\frac{74·70}{\lambda^2-0·1214}$ | | $\pm\frac{73·63}{\lambda^2-0·1348}$ | | $\pm\frac{76·47}{\lambda^2-0·1161}$ | |
| | $\lambda_0$ | 0·3457 | | 0·3413 | | 0·3485 | | 0·3672 | | 0·3408 | |
| Line. | | Obs. [α] | | Obs. [α] | | Obs. [α] | | Obs. [α] | | Obs. [α] | |
| | | d | l | d | l | d | l | d | l | d | l |
| $Cd_{5086}$ | | +581·3° | −581·3° | +587·1° | −588·1° | +555·4° | −554·9° | +553·8° | −552·8° | +536·5° | −535·5° |
| $Ag_{5209}$ | | 532·5 | 532·5 | 536·1 | 535·8 | 509·0 | 507·3 | 506·2 | 504·1 | 492·7 | 493·8 |
| $Hg_{5461}$ | | 452·5 | 450·0 | 456·5 | 457·1 | 430·0 | 428·4 | 426·2 | 425·5 | 418·0 | 420·0 |
| $Hg_{5780}$ | | 378·5 | 378·5 | 381·6 | 381·0 | 354·8 | 354·5 | 353·7 | 355·6 | 349·9 | 349·0 |
| $Na_{5893}$ | | 356·2 | 355·0 | 360·7 | 360·9 | 336·0 | 337·0 | 331·2 | 331·9 | 331·9 | 331·2 |
| $Li_{6103}$ | | 318·7 | 318·7 | 325·4 | 326·0 | 300·9 | 301·8 | 298·7 | 299·4 | 298·2 | 298·9 |
| $Cd_{6438}$ | | 273·7 | 275·0 | 280·0 | 279·7 | 257·3 | 258·1 | 256·5 | 256·3 | 255·7 | 256·3 |
| $Li_{6708}$ | | 245·0 | 243·8 | 250·0 | 248·5 | ... | ... | 229·5 | 229·5 | 228·4 | 228·3 |
| | | No mutarotation | | No mutarotation | | No mutarotation | | No mutarotation | | No mutarotation | |

## TABLE IV.

### o-*Acetoxyphenylaminomethylenecamphors.*

| Solvent : | | Ethyl alcohol. | | Methyl alcohol. | | Acetone. | |
|---|---|---|---|---|---|---|---|
| Conc. (g./100 c.c.) | *d* | 0·4000 | | 0·4004 | | 0·4012 | |
| | *l* | 0·4000 | | 0·4028 | | 0·4016 | |
| Calc | [α] | $\pm\frac{47{\cdot}20}{\lambda^2 - 0{\cdot}1213}$ | | $\pm\frac{53{\cdot}30}{\lambda^2 - 0{\cdot}0971}$ | | $\pm\frac{45{\cdot}26}{\lambda^2 - 0{\cdot}1201}$ | |
| | $\lambda^0$ | 0·3484 | | 0·3117 | | 0·3466 | |
| Line. | | Obs. [α] | | Obs. [α] | | Obs. [α] | |
| | | *d* | *l* | *d* | *l* | *d* | *l* |
| $Cd_{5086}$ | | ... | ... | +330·9° | −330·3° | +326·6° | −326·2° |
| $Ag_{5209}$ | | ... | ... | ... | ... | 299·1 | 300·1 |
| $Hg_{5460}$ | | +266·3° | −267·8° | 264·8 | 264·5 | 254·3 | 255·3 |
| $Hg_{5780}$ | | 221·3 | 221·3 | 224·8 | 224·8 | 211·9 | 211·6 |
| $Na_{5893}$ | | 208·7 | 207·5 | 212·3 | 213·5 | 199·4 | 199·2 |
| $Li_{6103}$ | | 187·5 | 187·5 | 193·5 | 194·9 | 179·4 | 178·1 |
| $Cd_{6438}$ | | 161·2 | 161·2 | ... | ... | ... | ... |
| $Li_{6708}$ | | 143·3 | 145·0 | 151·0 | 151·6 | 137·1 | 137·0 |

## TABLE V.

### m-*Acetoxyphenylaminomethylenecamphors.*

| Solvent : | | Ethyl alcohol. | | Methyl alcohol. | | Acetone. | |
|---|---|---|---|---|---|---|---|
| Conc. (g./100 c.c.) | *d* | 0·4024 | | 0·4024 | | 0·4008 | |
| | *l* | 0·4004 | | 0·4000 | | 0·4004 | |
| Calc | [α] | $\pm\frac{40{\cdot}38}{\lambda^2 - 0{\cdot}0748}$ | | $\pm\frac{42{\cdot}25}{\lambda^2 - 0{\cdot}0748}$ | | $\pm\frac{32{\cdot}15}{\lambda^2 - 0{\cdot}1193}$ | |
| | $\lambda_0$ | 0·2735 | | 0·2735 | | 0·3454 | |
| Line | | Obs. [α] | | Obs. [α] | | Obs. [α] | |
| | | *d* | *l* | *d* | *l* | *d* | *l* |
| $Cd_{5086}$ | | +220·0° | −220·0° | +228·2° | −228·3° | ... | ... |
| $Ag_{5209}$ | | 205·1 | 204.4 | 215·2 | 215·0 | ... | ... |
| $Hg_{5460}$ | | 181·1 | 181·1 | 189·1 | 189·1 | +180·9° | −182·3° |
| $Hg_{5780}$ | | 155·4 | 154·7 | 163·0 | 162·5 | 149·7 | 149·8 |
| $Na_{5893}$ | | 146·6 | 147·5 | 155·5 | 155·0 | 141·0 | 141·1 |
| $Li_{6103}$ | | 135·2 | 136·3 | 143·1 | 142·5 | 127·3 | 126·2 |
| $Cd_{6438}$ | | 119·4 | 117·5 | 124·4 | 125·0 | ... | ... |
| $Li_{6708}$ | | 108·1 | 107·4 | 113·1 | 113·7 | 97·1 | 97·4 |
| | | No mutarotation. | | No mutarotation. | | No mutarotation. | |

TABLE VI.

p-*Acetoxyphenylaminomethylenecamphor.*

| Solvent : | | Ethyl alcohol. | | Methyl alcohol. | | Pyridine. | |
|---|---|---|---|---|---|---|---|
| Conc. (g./100 c. c.) | *d* | 0·4020 | | 0·4008 | | 0·4036 | |
| | *l* | 0·4016 | | 0·4004 | | 0·4004 | |
| Calc. | [α] | $\pm\frac{38\cdot58}{\lambda^2-0\cdot0958}$ | | $\pm\frac{39\cdot23}{\lambda^2-0\cdot1040}$ | | $\pm\frac{41\cdot75}{\lambda^2-0\cdot0662}$ | |
| | $\lambda_0$ | 0·3095 | | 0·3225 | | 0·2573 | |
| Line | | Obs. [α] | | Obs. [α] | | Obs. [ ] | |
| | | *d* | *l* | *d* | *l* | *d* | *l* |
| $Cd'_{5085}$ ... | ... | +236·9° | −235·3° | ... | ... | +216·9° | −216·0° |
| $Ag_{5209}$ ... | ... | ... | ... | ... | ... | 204·5 | 204·4 |
| $Hg_{5460}$ ... | ... | 190·3 | 190·5 | +202·1° | −202·4° | 180·9 | 182·3 |
| $Hg_{5780}$ ... | ... | 162·9 | 161·9 | 172·2 | 172·4 | 154·4 | 153·6 |
| $Na_{5892}$ ... | ... | 153·0 | 153·6 | 161·0 | 159·8 | 148·8 | 148·6 |
| $Li_{6103}$ ... | ... | 139·3 | 138·2 | 146·0 | 144·9 | 136·4 | 134·9 |
| $Cd_{6438}$ ... | ... | 120·7 | 120·8 | ... | ... | . | ... |
| $Li_{6708}$ ... | ... | 112·0 | 112·1 | 113·6 | 112·4 | ... | ... |

No mutarotation

TABLE VII.

p-*Benzoxyphenylaminomethylene*-d-*camphor in ethyl alcohol.*

| Line. | α. | [α]. |
|---|---|---|
| $Cd_{5085}$ | ... 0·06° | ... 7·37° |
| $Hg_{5460}$ | ... 0·05 | ... 6·20 |
| $Hg_{5780}$ | ... 0·03 | ... 4·33 |
| $Na_{5892}$ | ... 0·02 | ... 2·48 |

A grateful acknowledgement is made to the Government of Bihar for the grant of a research scholarship to one of us (S. C. S.) which enabled him to take part in this investigation.

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# THE ALKALOID OF *RAUWOLFIA CANESCENS*, LINN. PART III. SOME DEGRADATION PRODUCTS OF RAUWOLSCINE

By (Miss) A. Mookerjee

Although rauwolscine, $C_{21}H_{26}O_3N_2$, is isomeric with and strikingly similar to yohimbine in its physical, chemical and physiological properties and in most of its degradation products, it differs from yohimbine in some respects. The third oxygen atom in rauwolscine is probably present as a hydroxyl group which is not reactive like that of yohimbine ; one of the nitrogen atoms is found to be secondary and the other tertiary and is attached to a ring. A skeletal formula of rauwolscine has been suggested after due considerations of several fragments like harman, 3-ethylindole, indole-2-carboxylic acid and isophthalic acid, isolated and identified from the degradation products of rauwolscine. Rauwolscinic acid does not undergo facile decarboxylation like yohimbic acid.

Rauwolscine, $C_{21}H_{26}O_3N_2$, the major alkaloid of *Rauwolfia canescens* (Mookerjee, *J. Indian Chem. Soc.*, 1941, **18**, 33) was previously reported to be allied to yohimbine both structurally (Mookerjee, *ibid.*, 1941, **18**, 485) and physiologically (Chakravarty, *Sciene and Culture*, 1941, **7**, 458). Like yohimbine it splits up on hydrolysis into methyl alcohol and a monobasic acid, called rauwolscinic acid $C_{20}H_{24}O_3N_2$, isomeric with yohimbic acid.

A comparative study of the absorption curves of both rauwolscine and yohimbine shows that the curves are similar to the curve of indole, pointing to the presence of an indole nucleus in rauwolscine molecule (*loc. cit.*). Yohimbine is known to possess an indole nucleus (Barger and Field, *J. Chem. Soc.*, 1915, **107**, 1025 ; Warnat, *Ber.*, 1926, **59**, 2891 ; 1927, **60**, 1118 ; Hahn and Just, *Ber.*, 1932, **65**, 717 ; Winterstein and Walter, *Helv. Chim. Acta*, 1933, **16**, 1343). The physical evidence of the presence of the indole nucleus in rauwolscine molecule has been confirmed by a study of some of the degradation products of the alkaloid, described in the present paper. The functions of all nitrogen and oxygen atoms have also been elucidated as far as possible and a skeleton formula has been proposed for the base, rauwolscine.

Rauwolscine with its two nitrogen atoms behaves as a monoacid base yielding a monohydrochloride, B,HCl, and an acid oxalate of the formula, $B,H_2C_2O_4$.

Rauwolscine can neither be brominated nor hydrogenated by means of (*a*) hydriodic acid (sp. gr. 1 7) and red phosphorus, (*b*) tin and hydrochloric acid, (*c*) sodium amalgam, and (*d*) catalytic hydrogenation. These facts indicate absence of unsaturation or of $-N=C-$linkage in rauwolscine molecule. No definite evidence could be obtained for the presence of a primary nitrogen atom. The iminomethyl determination was absolutely negative. As the absorption spectrum of the base is strongly suggestive of the presence of an indole nucleus, one of the nitrogen atoms must form part of the indole ring and hence does not normally respond to reactions characteristic of—NH—group. This assumption also explains the monoacidic character of rauwolscine. The second nitrogen atom is believed to be a tertiary one and in all probability forms part of a saturated ring or rings. This tertiary nitrogen atom probably accounts for the basic character of rauwolscine, the first nitrogen atom (or the indole) being very feebly basic. The presence of a --NH-CO group, which may readily explain the almost neutral character of the first nitrogen, is another possibility. But an amido-nitrogen along with the indole skeleton would have rendered rauwolscine far less basic than what it is. A monoacetyl derivative could, however, be obtained from rauwolscine by heating with acetic anhydride and fused sodium acetate. This is very likely *N*-acetyl derivative since indole, harman, harmaline, rutaecarpine and yohimbine etc., are known to yield *N*-acetyl derivatives, under similar conditions.

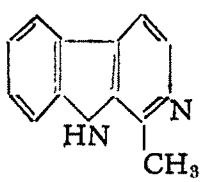
Two of the three oxygen atoms in rauwolscine molecule are present as carbomethoxy group as has already been proved (*loc. cit.*). The function of the third oxygen atom could not be ascertained easily since rauwolscine does not respond to the tests for aldehyde, ketone and alkyl ethers. No definite proofs for the presence of either alcoholic or phenolic hydroxyl group could be obtained as rauwolscine does not form *O*-methyl, or phthalic acid esters. Rauwolscine could not be converted into a chloro compound with phosphorous pentachloride, or into any unsaturated compound by the elimination of a molecule of water with dehydrating agents. The significance of the acetyl derivative is that it is indicative of the presence of an active hydrogen atom. The determination of active hydrogen in rauwolscine by Zerewitinoff's method shows the presence of two atoms of active hydrogen, one of which is apparently capable of undergoing acetylation. The second active hydrogen may possibly belong to a reactive methylene group, but the failure of rauwolscine and rauwolscinic acid to condense with acetone and anisaldehyde does not lend support to this hypothesis. The only possible way of accounting for this second active hydrogen, therefore, is to assume the presence of a hydroxyl group. These speculations lead one to the probability that rauwolscine contains NH group (as indole residue) and OH (alcoholic) group which, however, is more resistant to reactions than the one present in yohimbine, in as much as the latter yields a sulphuric ester and *O*-acetyl derivative (Barger and Field, *J. Chem. Soc.*, 1915 **107**, 1025 ; 1923, **123**, 1038), without any difficulty. The formula of rauwolscine, therefore, can be expanded to :

$$C_{19}H_{21}\left\{\begin{array}{l} -N \\ -NH \\ -OH \\ -CO_2Me \end{array}\right.$$

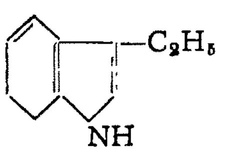
### *Pyrolysis of Rauwolscinic Acid.*

From the products of pyrolysis of rauwolscinic acid at 300°/4-5 mm., a strong base, m.p. 232°, and a neutral liquid have been isolated in pure condition.

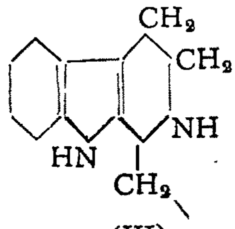
The solid base, which analyses for $C_{12}H_{10}N_2$, shows a pale blue fluorescence in aqueous solution, which deepened on the addition of concentrated hydrochloric acid. It is a monoacidic base, and yields a straw-yellow crystalline hydrochloride, $C_{12}H_{10}N_2$, HCl, m.p. 276°, (decomp.) and a bright yellow crystalline picrate, $C_{12}H_{10}N_2 . C_6H_2OH(NO_2)_3$, m.p. 256-58° (decomp.). The molecular formulae and physical properties of the base and its salts suggest its identity with harman (I), which is reported to melt at 232°, and produces a straw-coloured crystalline hydrochloride, m p. 276°, (decomp.) and a bright yellow picrate, m.p. 255° (decomp.).



(I)



(II)



(III)

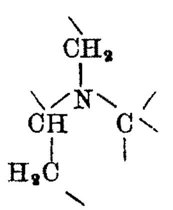
The identity is definitely established by mixed melting point with an authentic sample of harman prepared by the method of Kermack, Perkin and Robinson (*J. Chem. Soc.*, 1921, **119**, 1617).

The neutral product after final purification by distillation in vacuum is obtained as a mobile, colourless liquid which turns reddish brown in air. It has a fæcal odour like skatole and it turns a pine chip soaked in concentrated hydrochloric acid red. It produces ruby red crystalline picrate, m.p. 115-16°.

A comparison between the picrate of 3-ethylindole and that of the neutral liquid has been made, when they are observed to have similar physical properties. Further, no depression of melting point is observed when the two are mixed together. This fact establishes the constitution of the neutral compound as 3-ethylindole (II), which is apparently formed by further breakdown of the harman residue present in rauwolscine.

These degradation products confirm the presence of indole nucleus in rauwolscine and definitely establish not only the nature but also the relative positions of the two nitrogen atoms present in rauwolscine.

One would not, however, be justified to assume that harman molecule as such is present in rauwolscine and it is linked up with the rest of the molecule through a carbon atom of the pyridine nucleus. Such an assumption would not agree with the experimental observations, namely, (*i*) the production of 3-ethylindole and (*ii*) the absence of the tendency of rauwolscine to undergo reduction. On the other hand if the pyridine ring in rauwolscine is assumed to be reduced (corresponding to tetrahydroharman) (formula III), the formation of both harman and 3-ethylindole during pyrolysis is readily explained. This part formula is open to objection because of the presence of two $-NH-$ groups which cannot be reconciled with the observation that rauwolscine produces a monoacetyl derivative only. If, however, the assumption is made that union with the rest of the molecule has taken place through the nitrogen atom of the reduced pyridine as in formula (IV), no serious objection can be raised in interpreting the experimental results. Such a part formula would fully explain the differential behaviour of the two nitrogen atoms in rauwolscine, as also its fission into harman and 3-ethylindole. This portion (IV) is analogous to what is present in yohimbine. Accordingly rauwolscinic acid has been fused with solid potassium hydroxide at 300°, when besides harman, two different acids, one free from nitrogen and the other containing nitrogen atom, are isolated from the fusion product.



(IV)

The nitrogenous acid is obtained after careful purification involving high vacuum sublimation and by crystallisation in the final stages as shining flakes, m. p. 200-201°. The acid, when treated with soda lime, produces an oil. The latter has an offensive odour like skatole and turns pine chip moistened with concentrated hydrochloric acid red. The acid produces a violet-red colouration with isatin and concentrated sulphuric acid. The analytical data of the nitrogenous acid, $C_9H_7NO_2$, agreed with those of indole-monocarboxylic acid. That it is indole-2-carboxylic acid is conclusively proved by comparing it with a synthetic specimen, prepared according to the method of Ciamician and Zetti (*Ber.*, 1888, 21, 1930). There is no depression in mixed melting point and other properties are also found to be identical.

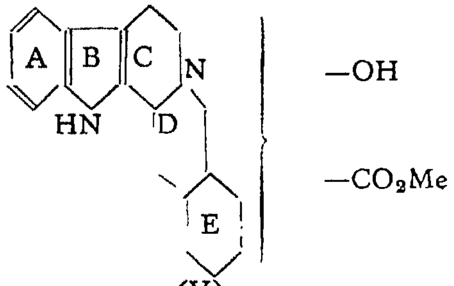
The nitrogen-free acid, after careful purification by repeated sublimation in *vacuo* and at ordinary pressure, is obtained as colourless shining needles, m. p. 328-30° (with sublimation). Its properties and analytical data correspond to those of *isophthalic* acid. The methyl ester of the degradation product melts at 68° and no depression in m. p. is observed when mixed with an authentic specimen of dimethyl ester of *isophthalic* acid, having m. p. 68·5°.

It has already been mentioned that rauwolscine exhibits a striking similarity to yohimbine in its properties both physical and chemical. It is found that rauwolscine resembles too in some of its degradation products with yohimbine and a table comparing their degradation products is drawn up below.

TABLE I.

| | Rauwolscine. | Yohimbine. |
|---|---|---|
| 1. Dry distillation ... | ... (a) Harman, m. p. 232° | ... (a) Harman, m. p. 232° |
| | (b) 3-Ethylindole $C_{10}H_{11}N$, liquid b p. 80°/0·1 mm. | ... (b) An unidentified indole derivative, m. p. 56°. |
| 2. Alkali fusion ... | ... (a) An unidentified indole derivative, liquid | (a) 3-Ethylindole, m. p. 32°. |
| | (b) Harman, m. p. 232° $C_{12}H_{10}N_2$. | (b) Tetrahydroyobyrine. $C_{19}H_{20}N_2$, m p. 167°. |
| | (c) Indole-2-carboxylic acid, $C_9H_7NO_2$, m p. 200-201°. | (c) Indole-2-carboxylic acid. $C_9H_7NO_2$, m p. 199-201°. |
| | (d) *iso*Phthalic acid, $C_8H_6O_4$, m p. 328-30°. (with sublimation). | (d) *m*-Toluic acid, $C_8H_8O_2$, m. p. 110°. |

It, therefore, appears that rauwolscine possesses *at least* four rings which correspond to A, B, C and E of yohimbine and the skeletal formula for rauwolscine appears to be (V).



(V)

The union of the cycloparaffin ring through the tertiary N atom as shown above is arbitrary, but appears probable in view of the similarity of degradation products obtained both from yohimbine and rauwolscine. Definite proofs for the presence of ring D in rauwolscine skeleton have yet to be obtained and the positions of hydroxyl and carbomethoxy groups have to be discussed. These will be the subject matter of a future communication.

## EXPERIMENTAL

*Acylation of Rauwolscine.*—Rauwolscine (0·25 g.) was boiled with acetic anhydride (5 c. c.) and freshly fused sodium acetate (0·25 g.) for 6 hours. The mixture was cooled and poured in a thin stream with constant stirring into ice-cold water (50 c. c.), when a brown, resinous matter separated, and was filtered off. The clear coloured filtrate was made ammoniacal, when the free acylated compound was precipitated; this was taken up in ether (80 c. c.) and the red ethereal solution was dried over anhydrous sodium sulphate. The residue on removal of ether was repeatedly crystallised from alcohol when globules of colourless solid, melting at 216-18° with decomposition were obtained. (Found in a specimen dried over $P_2O_5$ *in vacuo* for 2 hours at 125-30°: OMe, 7·41. $C_{21}H_{25}O_3N_2{\cdot}COCH_3$ requires OMe, 7·07 per cent).

*Hydrolysis of Monoacetylrauwolscine.*—Monoacetylrauwolscine (0·2g.) was boiled with aqueous sodium hydroxide (5 c. c.; 2*N*) for two hours. The pale red solution, thus obtained, was just acidified with acetic acid (2*N*) and the solid precipitate was collected, washed with ice-cold water and dried. The solid was then esterified with methyl alcohol and hydrogen chloride and kept overnight. Colourless needles separating were collected, dissolved in warm water, cooled in ice and made alkaline with liquor ammonia. Solids precipitated were crystallised from alcohol when they melted at 232° (decomp.) and showed no change in m. p when mixed with rauwolscine.

### *Determination of Active Hydrogen in Rauwolscine.*

The Zerewitinoff determination on a semi-micro scale by a modified apparatus of Flaschentrager gave the following consistent results:

(*a*) 0·0623 g. of rauwolscine in 2 c. c. dry pyridine yielded 9·3 c c. methane at 25° and 766 mm.

(*b*) 0·0681 g. of rauwolscine in 2 c. c. dry pyridine yielded 9·5 c. c. methane at 27° and 766 mm.

[Found (*a*) H, 0·59; (*b*) H. 0·596%. $C_{21}H_{26}O_3N_2$ requires for 2 active H, 0·57%].

*Dry Distillation of Rauwolscinic Acid.*—Rauwolscinic acid (2·5 g.) was heated in a metal-bath at 300° in vacuum (5 mm.). A thick brown product distilled over. The distillation was continued for half an hour when the pyrolysis was almost complete. The brown-red viscid distillate was extracted several times with ether (150 c. c. in all) and the ethereal solution (A) was shaken up with 1% hydrochloric acid (90 c. c. in 3 instalments). In this way the distillate was resolved into two fractions: (A) non-basic and (B) basic respectively.

*Isolation of 3-Ethylindole from the Fraction* (A).—The ethereal solution was washed with water and dried over anhydrous sodium sulphate. The residue obtained after evaporation of ether yielded on steam-distillation, a pale yellow oil with a fæcal smell. The aqueous distillate was extracted with ether when the oil passed into ethereal solution. The pale yellow ethereal extract, thus obtained, was dried over anhydrous sodium sulphate and ether removed. The residual brown oil distilled at 70-80°/0·1 mm. (yield, 0·1 g.).

The oil, when freshly distilled, was practically colourless, but slowly turned brown on exposure to air. The picrate of the oil was easily obtained on treating the components in benzene, as ruby-red needles, melting at 116-22°. On repeated crystallisations from benzene, red glistening needles, melting at 115-16°, were obtained. [Found in a specimen dried in *vacuo* at 100° for 4 hours over $P_2O_5$ : N, 14·85. $C_{10}H_{11}N. C_6H_2OH (NO_2)_3$ requires N, 14·97 per cent]. It showed no depression in m.p. when mixed with the picrate of a synthetic specimen of 3-ethylindole.

*Isolation of Harman from the Fraction* (B).—The well cooled, wine coloured hydrochloric acid extract, was basified with 5% sodium hydroxide solution when a semi-solid with resinous impurity separated out. It was taken up in ether and the red ethereal solution was washed with water and dried over anhydrous sodium sulphate. The ethereal extract was saturated with hydrochloric acid gas when a brown solid separated out. The yellow ethereal solution was decanted off and the solid mass was digested with warm water. The pale red solution was filtered from insoluble, resinous impurities, and basified with 5% sodium hydroxide solution. The base liberated was thrice subjected to the above process of purification (namely, alternate salt formation and liberation of the free base from the salts) and finally the viscous base was subjected to high vacuum distillation when a semi-crystalline product was obtained at 165-85°/0·1 mm. This was rapidly washed with ether when the adherent oil dissolved away leaving a colourless solid residue which on redistillation in high vacuum (165-85°/0·1 mm.) yielded a colourless solid (0·08 g.). It crystallised from benzene as shining needles, melting at 232°. The melting paoint did not change when the crystals were mixed with a sample of synthetic harman. (Found in a specimen dried in *vacuo* over $P_2O_5$ for 4 hours at 110° : C, 79·2; H, 5·43; N, 15·40. $C_{12}H_{10}N_2$ requires C, 79·11; H, 5·5; N, 15·39 per cent). Harman, thus obtained, was found to be freely soluble in alcohol, and sparingly in benzene and difficultly in water.

*The Hydrochloride of Harman.*—A solution of harman (0·05 g.) in hydrochloric acid (6 c.c.) deposited on concentration (2 c.c.) shining needles of the hydrochloride melting at 276-78° (decomp.). (Found in a specimen dried in *vacuo* over $P_2O_5$ for 4 hours : Cl, 16·18. $C_{12}H_{10}N_2$, HCl requires Cl, 16·25 per cent).

*The Picrate of Harman.*—The picrate of harman was obtained by the usual method from an ethereal solution of the components. It melted with decomposition at 258°, and its melting point did not change when mixed with a specimen of the picrate of synthetic harman. [Found in a dry specimen : N, 17·08. $C_{12}H_{10}N_2$, $C_6H_2OH (NO_2)_3$ requires N, 17·03 per cent].

*Preparation of Harman.*—In synthesising harman, the method of Kermack, Perkin and Robinson was followed with a slight modification to improve the yield of the product. The tryptophan solution (0·5 g.) in water (150 c.c.) was refluxed with ice-water in the condenser for 2 hours with an aqueous solution (25%) of freshly prepared acetaldehyde (10 c.c.) and then boiled with a 10% aqueous solution of potassium dichromate (25 c.c.) for another ½ hour. Sulphur dioxide gas was bubbled through the mixture after cooling. The mixture was afterwards boiled to remove excess of sulphurous acid and treated with an aqueous solution of sodium carbonate, till faintly alkaline. The precipitate of chromium hydroxide was filtered and repeatedly washed with boiling water. The filtrate and the washings (400 c.c.) were acidified with hydrochloric acid, and concentrated (20 c.c.) and then basified with 10% aqueous solution of sodium hydroxide at 0°, when colourless flakes of harman were obtained. The flakes crystallised from benzene as lustrous needles, m.p. 232° (yield 0·40 g).

*Fusion of Rauwolscinic acid with Potassium Hydroxide.*—Rauwolscinic acid (2·5 g.) was fused with solid potassium hydroxide (15 g.) in a nickel crucible heated to 300° on a metal-bath. The fused mass was stirred constantly to prevent frothing of the molten mass, due to the evolution of ammonia gas. When the evolution of the gas had stopped, the mass was allowed to cool and then lixiviated with water (100 c.c.). The product was saturated with ammonium chloride to decompose excess of potassium hydroxide. The solution was filtered and the filtrate was extracted with ether. In this way ether soluble products (C) were removed.

The alkaline aqueous solution, containing acidic degradation products, was then acidified with hydrochloric acid when a pale yellow viscid mass separated and was drawn into ether. The ether solution was well washed with water and then treated with an aqueous solution of potassium hydroxide (1%). The latter was drawn out, extracted with ether to remove gummy matters and acidified with hydrochloric acid, when a viscid substance separated. This was purified by repeating the process three times. The pasty acid finally obtained was fractionally sublimed in vacuum when two fractions, (D) and (E), were obtained. Fraction D distilled at 110-115°/0·1 mm. and Fraction E at 160-180°/0·1 mm.

*Isolation of Indole-2-carboxylic Acid from the Fraction* (D).—The ethereal solution of the fraction (D) was repeatedly extracted with a solution of sodium bicarbonate (2*N*). The aqueous extract was cooled in ice and then acidified with hydrochloric acid. The precipitate, thus obtained, was taken up in ether. The ethereal solution was well washed with water and dried over anhydrous sodium sulphate. The solid residue, obtained after the removal of ether, was soxhletted with petroleum ether (50 c.c. ; b.p. 30-50°) for about 8 hours, when the residue almost completely went in solution. The petroleum ether extract was concentrated to 10 c.c. and on being left overnight deposited almost colourless leaflets, m. p. 198-99°. These were further purified by crystallising first from benzene and finally from a mixture of ether and petroleum ether as shining flakes, m.p. 200-201° (yield 0·4 g.). (Found in a dry specimen : C, 67·07 ; H, 4, 35 ; N, 8·7. $C_9H_7O_2N$ requires C, 67·21 ; H, 4·53 ; N, 8·87 per cent). The compound did not show any depression in melting point when mixed with a synthetic specimen of indole-2-carboxylic acid. The degradation product like indole-2-carboxylic acid gave a red-violet colouration with isatin in concentrated sulphuric acid. On heating to 230°, it decomposed producing an oil, which had the offensive small of indole and which turned pine chips moistened with hydrochloric acid red.

Indole-2-carboxylic acid required for identification was prepared from 2-methylindole by fusion with caustic potash according to the method of Ciamician and Zetti (*Ber.*, 1888, 21, 1930).

*Isolation of isoPhthalic Acid from the Fraction* (E).—The pale yellow sublimate (obtained at 160-80°/0·1 mm.) was purified by resublimation at 310-15° at the ordinary pressure. The colourless sublimate was further purified by dissolving it in a solution of sodium bicarbonate, filtering the solution and reprecipitation by means of hydrochloric acid. It was then taken up in ether. The residue on removal of the solvent was thrice sublimed as before at 310-15°. The pure sublimate was slightly acidic to litmus and melted at 330°. It crystallised from water in shining flakes, m.p. 330° (sublimation). (Found in a specimen dried in *vacuo* over $P_2O_5$ for 4 hours: C, 57·65; H, 3·81. $C_8H_6O_4$ requires C, 57·83; H, 3·90 per cent). The acid showed no depression in melting point when mixed with synthetic *iso*phthalic acid, which was prepared by permanganate oxidation of an authentic specimen of *m*-toluic acid and which alone also melted at the same temperature.

*Dimethyl Ester of the* iso*Phthalic Acid obtained by Potash Fusion.*—The methyl ester was prepared by treating an ethereal solution of the acid (0·006 g.) with diazomethane in ether. The residue after removal of ether was an oil which distilled at 90°/0·1 mm. The distillate solidified on cooling and was crystallised from petroleum ether (b. p. 50-60°) in shining needles. The methyl ester melted at 68·5°, and showed no change in m.p. when mixed with a specimen of dimethyl ester of *iso*phthalic acid which alone melted at 68·5°.

*Isolation of Harman from the Ether Extract* (C).—The red coloured ethereal solution, obtained from potassium hydroxide fusion products of rauwolscinic acid, was treated with hydrochloric acid when the acid layer (F) became red and the ether layer (G) pale yellow.

1. *Treatment of the Acid Layer* (F).—The acid solution yielded a white precipitate on basification. The precipitate was extracted with ether and on removal of ether it was recovered as a semi-solid mass, from which on treatment with hydrochloric acid, straw-yellow coloured needles, melting at 278-80° (decomp.) were obtained. The needles were purified by repeated crystallisation from water. An aqueous solution of the purified product, when made ammoniacal, deposited colourless flakes, which crystallised from benzene as shining needles, m.p. 230-31°. (Found in a specimen dried in *vacuo* over $P_2O_5$ for 4 hours at 110°: C, 79·25; H, 5·42; N, 15·45. $C_{12}H_{10}N_2$ requires C, 79·00; H, 5·5; N, 15·39 per cent). They showed no depression in melting point when mixed with an authentic specimen of harman.

*Picrate of the base.*—The picrate was obtained by the method previously described and had m.p. 258°, (decomp.). [Found in a dry specimen: N, 17·1. $C_{12}H_{10}N_2$. $C\ H_2OH(NO_2)_3$ requires, N, 17·03 per cent].

2. *Treatment of the ether layer* (G).—The oily residue (0·005 g.) obtained after the removal of ether had an indole-like faecal odour, and responded to the tests of an indole (pine chip reaction). Neither the residue nor its derivatives could be obtained in a solid state to facilitate further examinations.

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# COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART IV. PALLADIUM BIGUANIDINE AND ITS SALTS

By Priyadaranjan Ray and Sailaja Prasad Ghose

Palladium is known to resemble nickel in many of its chemical properties and possesses like the latter an electronic structure of the pseudo-inert gas type. It was, therefore, considered worthwhile to study the preparation and properties of palladium biguanide complexes and compare them with those of nickel. Besides palladium biguanidine and its hydroxide, a number of other salts, namely, chloride, bromide, iodide, sulphate, thiosulphate, thiocyanate, nitrate, palladothiocyanate, chloropalladite and chloroplatinate have been described in this paper. The palladium biguanide complex resembles the corresponding nickel complex, but is more stable and comparatively less soluble. The complex thiocyanate undergoes an interesting disproportionation in presence of acid to form palladium biguanidinium palladothiocyanate.

In parts I and II of this series, copper and nickel biguanidines and their salts have been described (Rây and Bagchi, *J. Indian Chem. Soc.*, 1939, **16**, 617 ; Rây and Purakayastha, *ibid.*, 1941, **18**, 217). As nickel and palladium resemble each other in many of their chemical properties and possess an electronic structure of pseudo-inert gas type, it was naturally expected that complex palladium biguanide compounds, similar to those of nickel, could be readily obtained. The present paper deals with the preparation and properties of these compounds. Besides palladium biguanidine and its hydroxides, a number of palladium biguanidinium salts, *viz.*, chloride, bromide, iodide, sulphate, thiosulphate, nitrate, thiocyanate, palladothiocyanate, chloropalladite and chloroplatinate, have been prepared. Their solubility and other properties follow the corresponding nickel compounds, but are somewhat more intensified regarding their complex character. In other words, the palladium complexes are relatively more stable and less soluble than their nickel analogues. The palladium biguanide complex is light yellow in colour and diamagnetic. Hence, like the corresponding nickel complex it is believed to possess a planar configuration with $dsp^2$ hybrid bonds.

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The light yellow palladium biguanidinium thiocyanate in presence of a little acid suffers an interesting disproportionation giving rise to palladium biguanidinium palladothiocyanate (reddish brown) with partial elimination of biguanide.

$$2[\mathrm{Pd}\,(\mathrm{BigH^+})_2](\mathrm{SCN})_2 + 2\,\mathrm{HCl} = [\mathrm{Pd}\,(\mathrm{BigH^+})_2]\ \mathrm{Pd}\,(\mathrm{SCN})_4 + 2\ \mathrm{BigH.HCl}$$

(BigH = a biguanide molecule, $C_2N_5H_7$).

## EXPERIMENTAL

*Palladium* bis*Biguanidinium Hydroxide.*—Fine, silky, light yellow crystals of of the complex base were precipitated by the addition of palladous chloride solution to that of biguanide sulphate in an excess of alkali. It was washed first by decantation with cold water, then with alcohol and finally dried in air free from $CO_2$. {Found: N, 41·51; Pd, 31·42. $[Pd\,(BigH^+)_2]\,(OH)_2$ requires N, 40·85; Pd, 31·13 per cent}. Magnetic susceptibility, $\chi_m = 0{\cdot}259 \times 10^{-6}$.

*Palladium* bis*Biguanidine.*—When the above hydroxide was heated to 115° it lost 10·52% of its weight and changed into anhydro base. {Found: Pd, 34·72. $[Pd\,(C_2N_5H_6)_2]$ requires Pd, 34·78 per cent}.

*Palladium* bis*Biguanidinium Chloride.*—A light yellow solution of the chloride was obtained by neutralising the complex hydroxide, suspended in water, with 2*N*-HCl. On cooling, the light yellow crystals of the chloride separated out. These were washed first with a little ice-cold water, then with alcohol and finally dried in air. The substance can also be obtained by the action of ammonium chloride on the complex base. {Found: Cl, 17·11; Pd, 25·55. $[Pd\,(BigH^+)_2]\,Cl_2 \cdot 2H_2O$ requires Cl, 17·06; Pd, 25·67 per cent}.

*Equivalent conductivity at* 28°.

| $v$ (litres) | ... | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\lambda_v$ | ... | 103·68 | 108·80 | 111·30 | 113·45 | 113·88 |

$\lambda_\infty$ (mean) = 120·76 from Walden's formula.

The mobility of 1/2 $[Pd\,(BigH^+)_2] = 120{\cdot}76 - 79{\cdot}33 = 41{\cdot}43$, the mobility of chlorine ion at 28° being 79·33. The value for the corresponding Ni-complex ion at 25° (Rây and Purakayastha, *loc. cit.*) is equal to 46·27. On making necessary correction for the temperature difference it will be found that the mobility of the complex palladium biguanide ion is considerably lower than that of its nickel analogue. This is in agreement with their respective atomic radius. The values of their atomic radii, according to Goldschidt, are $Ni = 1{\cdot}244 \times 10^{-8}$ cm. and $Pd = 1{\cdot}370 \times 10^{-8}$ cm. respectively.

*The bromide* was prepared by adding a strong solution of potassium bromide to that of the complex chloride. It forms light yellow crystals moderately soluble in water. {Found: Br, 33·02; Pd, 21·80. $[Pd(BigH^+)_2]Br_2.H_2O$ requires Br, 32·86; Pd, 21·94 per cent}.

*The iodide* was prepared in the same way as the bromide using potassium iodide. Recrystallised from water it forms light yellow crystals, moderately soluble in water, but freely soluble in alcohol. The colour of the substance changes gradually to light

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brown, possibly with slight decomposition. {Found: N, 23·55; I, 42·45; Pd, 17·95; $H_2O$ (by loss at 105°), 6·03. $[Pd\ (BigH^+)_2]I_2 .\ 2H_2O$ requires N, 23·39; I, 42·41; Pd, 17·82; $H_2O$, 6·3 per cent}.

*Sulphate*—Yellowish white, curdy precipitate of the sulphate was obtained by adding a solution of potassium sulphate to that of the complex chloride. The substance is almost insoluble in water. {Found: N, 30·98; Pd, 23·02; $SO_4$, 20·79. $[Pd\ (BigH^+)_2]\ SO_4.3H_2O$ requires N, 30·53; Pd, 23·26; $SO_4$, 20·92 per cent}.

*Thiosulphate.*—Practically insoluble, curdy, light buff-coloured precipitate of the thiosulphate was obtained by adding a solution of sodium thiosulphate to that of the complex chloride. The substance is not acted upon by dilute alkalis. {Found: S, 13·62; Pd, 22·55. $[Pd(BigH^+)_2]\ S_2O_3.3H_2O$ requires S, 13·49; Pd, 22·49 per cent}.

*The nitrate* was obtained as a yellowish white, crystalline precipitate when a solution of potassium nitrate was added to that of the complex chloride. It was purified by recrystallisation from hot water. {Found: Pd, 24·58; $NO_3$, 28·23. $[Pd\ (BigH^+)_2](NO_3)_2$ requires Pd, 24·65; $NO_3$, 28·65 per cent}.

*Thiocyanate.*—When a strong solution of potassium thiocyanate was added to that of the complex chloride, very light yellow, silky needles of the complex thiocyanate separated out. This was recrystallised from water, washed with ice-cold water and dried in air. The substance is highly soluble in alcohol. In presence of a little acid it changes into a light brown, insoluble product described below. {Found S, 14·50; Pd, 24·05. $[Pd(BigH^+)_2](SCN)_2.H_2O$ requires S, 14·45; Pd, 24·10 per cent}.

*Palladothiocyanate.*—As stated above it results from the action of dilute acids upon the previous compound. It was also prepared by the addition of a solution of potassium palladothiocyanate to that of the complex chloride. The substance forms red-brown, silky crystals, insoluble in water. {Found: N, 30·52; S, 19·54, 19·70; Pd, 33·06, 33·04. $[Pd\ (BigH^+)_2]\ Pd\ (SCN)_4$ requires N, 30·27; S, 19·77; Pd, 32·96 per cent}.

*Chloropalladite.*—When a solution of potassium palladochloride was added to that of the complex chloride, the light yellow crystals, changing to brownish yellow, of the complex chloropalladite separated out. These were washed with ice-cold water and dried over conc. $H_2SO_4$. It dissolves in hot water with decomposition. It is soluble in alcohol. {Found: Cl, 25·30; Pd, 38·31. $[Pd(BigH^+)_2]\ PdCl_4$ requires Cl, 25·45; Pd, 38·38 per cent}.

*The chloroplatinate* was obtained as a bright yellow, insoluble precipitate by adding a solution of sodium chloroplatinate to that of the complex chloride. {Found: Cl, 26·46; Pd, 13·25; Pt, 24·12. $[Pd(Big\ H^+)_2]\ PtCl_6.5H_2O$ requires, Cl, 26·37; Pd, 13·22; Pt, 24·19 per cent}.

The palladium biguanide complex also forms interesting polyhalides, which will be described in a separate paper.

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# ESTIMATION OF SOME OF THE AMINO-ACIDS IN COBRA (*NAJA NAJA*) NEUROTOXIN

By B. N. Ghosh and D. K. Chaudhuri

A highly toxic substance which paralyses the respiratory movements but has no action on heart, has been isolated form cobra venom. The diamino-acids contained in this active principle has been estimated. It has been found that the composition of this active principle is similar to that of thymus histone

It has been reported in a previous communication by Ghosh and De (*Indian J. Med. Res*, 1938, 25, 784) that the iso-electric point of the cobra-neurotoxin lies above *p*H 8·0. It may be inferred from this observation that the neurotoxin has got basic properties and probably belongs to the class of proteins known as histones or protamines. Since the basic properties of the histones and protamines have been traced to the relatively high proportion of the diamino-acids contained in their molecules, an estimation of these amino-acids in the cobra-neurotoxin may lead to valuable information regarding its chemical nature. With this object in view, the neurotoxin was separated from the various constituents such as trypsin, haemolysin, choline esterase, etc. which are present in the crude cobra venom. The preparation which we finally obtained was weight for weight, about 15 times more toxic than the crude venom with which we started. The toxicity of this neurotoxin could not be further increased either by fractional precipitation with electrolytes or by cataphoretic experiments in a multi-chambered cell. This neurotoxin produces stoppage of respiratory movements, but it has no action on heart. It will be referred to as neurotoxin (R). The diamino-acids of the crude cobra venom were also estimated for the purpose of comparison, as it would indicate how the composition changed with the increase in purity of the neurotoxin. The results are recorded in this paper. The sample of crude venom used in this experiment was highly toxic and its m.l.d. for pigeons (300. g.) was 0·095 mg.

## EXPERIMENTAL

*Isolation of the Neurotoxin (R).*—The crude cobra venom contains, besides the neurotoxin, other active principles like the haemolysin and also a considerable amount of inactive proteins. It was found by experiment that the major portion of these latter substances could be removed by fractional precipitation with sodium sulphate. A stock solution of sodium sulphate was prepared for this purpose using 44g. of anhydrous sodium sulphate per 100 c.c. of water at 37° and the precipitation was carried out in two steps using different concentrations of sodium sulphate. In the first step (*a*), 300 c.c. of a 0·5% solution of the cobra venom were added with constant stirring to an equal volume of the sodium sulphate and the mixtute was incubated at 37° for 30 minutes. It was then filtered, the precipitate dissolved in 150 c.c. of water and reprecipitated by the addition of 150 c.c. of the sodium sulphate solution. This process was repeated once more and the different filtrates were combined. The combined filtrate was found to contain more than 80%

of the neurotoxin. The next step (*b*) consisted of further fractionation of this combined filtrate. The volume of the filtrate was measured and for every 200 c.c., 100 c.c. of the sodium sulphate solution were added with constant stirring. The mixture was left in a thermostat at 37° for 30 minutes and then filtered. The precipitate was disolved in 200 c.c. of water and then treated with 420 c.c. of sodium sulphate solution. After incubarion at 37° for 30 minutes, it was filtered. The filtrates were combined and this mixture was found to contain about 56% neurotoxin.

The volume of the combined filtrate was measured and to every 100 c.c. of the filtrate 3·3 c.c. of 2/3 *N*-sulphuric acid and 3·3 c.c. of 10% solution of sodium tungstate were added with constant stirring. The mixture was left at room temperature for about 10 to 15 minutes and then centrifuged. The supernatant liquid was decanted off and the precipitate washed twice by centrifugalisation using each time 30 c.c. of an aqueous solution of sodium tungstate and sulphuric acid, in the same proportion in which they were used previously. After the washing was completed, the precipitate was suspended in 30 c.c. of water and *N*/5-sodium hydroxide solution was added to it drop by drop with repeated stirring until the solution became alkaline (*p*H 8·6 to 8·8). To this solution was then added barium chloride in slight excess to remove the tungstic acid as insoluble barium tungstate. The mixture was centrifuged and the supernatant liquid containing the neurotoxin was withdrawn. It was neutralised with dilute sulphuric acid solution and any barium ions contained in the solution were removed by treatment with just sufficient quantity of dilute sodium sulphate solution. It was filtered, the filtrate cooled in an ice-chest and then treated with three times its volume of ice-cold methyl alcohol when a precipitate was formed containing the neurotoxin. The mixture was centrifuged, the supernatant liquid was decanted off and the precipitate dried in a vacuum desiccator.

The dried substance was dissolved in water, cooled to about 2° and subjected to fractional precipitation between *p*H 1·8 and *p*H 2·0, with ice-cold methyl alcohol. The experiments were carried out at a low temperature in order to avoid destruction of the neurotoxin owing to denaturation. It was noticed that when a volume of alcohol equal to 1·8 times that of the aqueous solution was used, a precipitate was formed which had the highest toxicity per unit weight. The precipitate obtained under the above condition was washed several times by centrifugalisation, using a mixture of methyl alcohol and water in the proportion of two volumes of alcohol to one volume of water. Finally it was washed with absolute methyl alcohol and dried in a vacuum desiccator. This dried substance will be referred to as neurotoxin (R). The minimnm lethal dose for pigeons of this neurotoxin (R) was found to be 0·0064 mg. only.

## *Hydrolysis of the Neurotoxin.*

The separation and estimation of the basic amino-acids were carried out by the method of Kossell and Kutscher (Kossell, "The Protamines and Histones", 1927, p. 4, ; *Physiol. Chem.*, 1900, 31, 165) A weighed quantity of the material not exceeding 0·5g. was digested with 10 c.c. of 30% (by weight) sulphuric acid in a conical flask fitted with a reflux condenser and the flask was placed in an oil-bath maintained at a temperature of about 130° to 140°. The digestion was continued for 18 hours, as preliminary experiments showed that this period was required for completing the hydrolysis. After cooling, the volume was made up to 50 c.c. and 40 c.c. of it were used for the estimation of the diamino-acids and 5 c.c. for the estimation of total amino-acid nitrogen after the removal of the humin matter by centrifuging.

### *Estimation of Histidine, Arginine and Lysine.*

40 C.c. of the hydrolysate were neutralised with concentrated baryta and again filtered. The combined filtrate was evaporated to 20 c.c. and divided into two equal parts each of which was separately analysed for its histidine, arginine and lysine content by the method of Kossel and Kutscher (*loc. cit.*). The results are recorded in Table I.

TABLE I.

| Substance. | Nitrogen as per cent of total nitrogen. | | |
|---|---|---|---|
| | Arginine. | Histidine. | Lysine. |
| Dry crude cobra venom ... ... | 7·7 | 4·1 | 14·2 |
| Purified cobra neurotoxin ... ... | 28·5 | 7·3 | 5·2 |
| Thymus histone ... ... | 27·1 | 5·8 | 8·04 |
| Histopeptone from thymus ... ... | 28·4 | 2·9 | 12·1 |

## DISCUSSION.

It will be noticed from the data recorded in Table I that the neurotoxin (R) which we have isolated from cobra venom (*Naja Naja*) is similar to thymus histone, in so far as its composition with respect to arginine, histidine and lysine is concerned. It will also be noticed that while the neurotoxin is rich in arginine the crude cobra venom is rich in lysine. It is, therefore, worth investigating which of the active principles of cobra venom is rich in lysine. Further work on this line is in progress.

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# CHARGE AND STABILITY OF COLLOIDS. PART I. ADSORPTION OF OPPOSITELY CHARGED IONS UNDER DIFFERENT CONDITIONS

By B. P. Yadava and A. C. Chatterji

The amount of the precipitating ion adsorbed to neutralise the charge on a colloid has been measured. A distinction has been drawn between "chemical adsorption" which is the amount of the precipitating ion required to neutralise the charge on a colloid alone, and the "physical adsorption" which is the amount of the precipitating ion adsorbed by the coagulum. In an ordinary coagulation experiment by an electrolyte, the amount of the precipitating ion, which is carried down, is the sum total of these two. From the amount of the "chemical adsorption" alone, the charge on the colloidal particles has been calcultaed by a method similar to that used by Burton with certain modifications.

Various authors (Weiser, *J. Phys. Chem.*, 1925, **29**, 255 ; Dhar, *J. Phys. Chem.*, 1930, **34**, 326) have said that the amount of the precipitating ion carried down by the coagulated mass of a colloid is due to (*a*) the amount of adsorption necessary to produce charge neutralisation and (*b*) the adsorption by the electrically neutral particles during the process of agglomeration.

Burton (*Phil. Mag.*, 1906, **12**, 425) attempted to measure the charge on a colloid by finding out the amount of aluminium ions adsorbed by a given amount of a silver colloid. The method employed was to measure the cataphoretic velocity of the colloidal particles when different concentrations of $Al_2(SO_4)_3$ were added to the sol. The silver particles ceased to move towards the anode and began to move towards the cathode. Burton derermined the critical concentration of the aluminium ions required for coagulation by plotting the curve and noting graphically the critical concentration of aluminium ions when the velocity was zero. Here Burton assumed, as pointed out by Lewis, that the whole of the aluminium was adsorbed by the colloid. He also neglected the adsorption under (*b*). Lewis has calculated the charge from Burton's data and found it to be $2{\cdot}8\times10^{-3}$ e. s. u.

By utilising the Helmholtz-Lamb theory of double layer, Lewis (*Kolloid Z.*, 1909, **4**, 211) has determined the charge on an oil-emulsion in water by measuring the velocity of the particles under a potential gradient, and he obtained the value $e = 4\times10^{-4}$ e. s. u. Again taking platinum colloid in water, Lewis has calculated $e$ to be $8\times10^{-5}$ e. s. u., by applying Lamb's equation to Burton's results. Lewis admits that the value of *d*, the thickness of the double layer, taken from Helmholtz's approximate value, may increase as much as ten times which certainly would reduce the value of $e$ by ten times. Lewis made another attempt to determine the value of $e$ by applying Stoke's law to the motion of the colloidal particle in an electric field. Taking the case of a silver colloid and utilising Burton's data, Lewis found $e = 8\times10^{-8}$ e. s. u. There is no doubt, therefore, that Burton's result for silver particles calculated from the adsorption of $Al^{\cdots}$ ions is much too large.

The high value obtained by Burton may be due to the following two causes :

(*i*) He assumed that all the aluminium ions added to coagulate the colloid were adsorbed. Here it is necessary to determine the actual adsorption of the coagulating ions.

(*ii*) In calculating the charge by Burton's method it is also necessary to take into account the adsorption due to the first cause only and not due to the second.

Dhar (*loc. cit.*) has assumed that the adsorption under (*b*) is due to the residual affinity of the uncharged surface. Whilst this factor is the main cause, others may also produce adsorption, such as ions used in mechanically blocking the pores and entrainment of precipitating ions during agglomeration (Mukherjee, Chaudhury and Ghosh, *Trans. Nat. Inst. Sci. India*, 1935, 1, 47).

In our experimental calculations of the amounts of adsorption under (*b*) we have not taken into consideration the adsorption due to these other factors—which is bound to be small.

The diffused double layer consists of the ionised part of the ion pairs at the surface together with diffused ionised portion in the dispersion medium, a part of which is osmotically active. The portion of the double layer held on the surface gives a net charge to the colloid and was originally assumed to be responsible to give stability. Conditions of unstability were studied by following the variations in the charge on the surface.

We have measured the adsorption of ions of an added electrolyte which carry a charge opposite to that of the colloid. In effect the adsorption of these oppositely charged ions releases other ions of the same sign from the counter part of the double layer. A quantitative relation between the adsorbed ions and the ions displaced may or may not exist. In subsequent parts of this series it has been found out that no simple relation exists between the amount of the added ions and the quantity of the released counter ions. It must, however, be pointed out that the ions released may not all come from the counter part of the double layer. Some of them may even be released from the surface of the colloid where they might be electrically held.

But in this paper, while calculating the charge, it has been assumed that the adsorbed ions displace all the ions of the same sign which form the outer portion of the double layer and thus the amount of the oppositely charged ion adsorbed is a measure of the amount of ions in the primary adsorbed layer.

We are fully alive to the limitations of the above assumptions but the order of the charge determined bears a close relation to the order of the charge determined by other methods. The aim of this paper is to show that with suitable precautions, which may be only a first approximation, a method depending on the basic idea of Burton may be evolved which gives results in conformity with the results obtained by other methods.

The adsorption taking place under (*a*) which is due to charge neutralisation, has been termed "chemical adsorption" and that taking place under (*b*) has been termed "physical adsotption". We are aware that expressions "chemical and physical adsorptions" have been used in different senses than stated above, *e.g.*, "chemical adsorption" in the sense of chemisorption of Zsigmondy and "physical adsorption" in the sense of mechanical blocking of the pores. Our reason for calling the adsorption under (*a*) as the "chemical adsorption" is that adsorption which takes place here is due to charge neutralisation, and in case of adsorption as well as peptisation, a close relationship is present if not a too rapid change takes place from electrostatic to pure chemical combination" (Kolthoff, "Mass Analyse", I. p. 167).

In calculating the charge on a colloid we have tried to eliminate the adsorption under (*b*) by estimating the adsorption with freshly prepared and thoroughly washed neutral precipitates originally produced in the presence of electrolytes. While this gives a large amount of adsorption taking place under (*b*) during coagulation, the procedure is not free from inherent defects. In the first place, the adsorption by surfaces during the course of formation is bound to be greater than when they have been formed. Moreover, the amount of the neutral surface during coagulation is bound to be more than in an equal weight of freshly formed precipitate. Due to the above causes adsorption under (*b*) should be more than the adsorption by the freshly formed precipitate. Also, the use of KCl with ferric hydroxide sol and of HCl with $As_2S_3$ sol to produce the fresh precipitates is not free from difficulties. During coagulation oppositely charged ions from these electrolytes are adsorbed and it is just possible that they might not be completely removed by washing even when the filtrate shows no sign of them. This will certainly produce a lesser amount of the so-called "physical adsorption" under (*b*). Inspite of these difficulties we are of opinion that the experimental procedure gives good results as a first approximation, and certainly gives a very fair idea of "chemical adsorption" under various conditions as the defects in determining "physical adsorption" are common to all experiments.

Recently in addition to chemical method, E. M. F. measurements and radioactive indicators have been used by Freundlich (*Z. physikal. Chem.*, 1929, **141**, 249) and Kolthoff (*J. Amer. Chem. Soc.*, 1933, **55**, 2657) to measure the amount of adsorption by colloids. In the case of E. M. F. method, activities instead of concentrations were taken into consideration while determining adsorption. This involves difficulties. Moreover, this method has its limitations and cannot be used accurately for all the electrodes. The radio-active indicator method gives a result which can be accurately determined within 2% of the total adsorption (Kolthoff and Rosenblum, *J. Amer. Chem. Soc.*, 1933 **55**, 2657). Adsorption indicators also give results within 2%. The chemical analysis can be made quite sensitive when the amount of the meterial used is sufficiently large. The radio-active indicators are very useful when adsorption is to be determined from a very dilute solution, but in cases in which solutions are sufficiently concentrated, analytical methods are quite satisfactory.

## EXPERIMENTAL

A large volume of colloidal solution (500 c. c.) was taken and the portion of the precipitating ion that was adsorbed was determined by chemical analysis at the coagulating concentration. The part of the precipitating ion that was thus adsorbed represented the total adsorption. The "physical adsorption" was determined by taking an equal amount of the sol and precipitating by adding HCl to $As_2S_3$ and KCl to $Fe(OH)_3$ sol, and then thoroughly washing it till free from chlorine, and adding the calculated amount of the coagulating electrolyte and other ingredients where necessary and determining the amount of the precipitating ion adsorbed by the coagulum, under the same conditions as in the coagulation experiments.

*Preparation of the Colloidal Solutions.*—$As_2S_3$ sol was prepared by dissolving Kahlbaum's analytically pure arsenious oxide in freshly distilled water so as to give a concentrarion of the sol of about 15 to 20 g. per litre. The solution was filtered and a slow current of $H_2S$ was passed till saturated. Excess of $H_2S$ was removed by passing a current of pure hydrogen

Ferric hydroxide sol was prepared by dissolving chemically pure ferric chloride (50 g.) in 4 litres of distilled water to which dilute ammonia was added drop by drop. The solution was shaken after addition of each drop of ammonia, till the solution was just short of precipitation. The sol was then kept for dialysis.

The concentration of $As_2S_3$ sol was determined directly by evaporating 10 c. c. of the sol in a silica crucible by keeping in an electric oven at 110° and weighing.

The ferric oxide in 25 c. c. portion of the sol was coagulated by ammonia, and the precipitate was collected, washed, ignited and weighed in the usual manner. The dialysed $Fe(OH)_3$ sol was used in the course of this investigation. The chlorine content of 25 c. c. portion of the sol was obtained first by adding a certain quantity of halogen free nitric acid and heating. This process dissolves the oxide leaving a precipitate of silver chloride. After this the silver salt was collected in a sintered crucible dried at 110° in an electric oven and weighed (*cf.* Weiser, *J. Phys. Chem.*, 1931, **35**, 7).

*Determination of the Coagulating Concentration of the Electrolytes.*—From a series of preliminary experiments, the coagulating concentrations of the electrolytes were determined by taking 5 c. c. of the sol and adding to it the necessary quantity of the coagulating electrolyte, keeping the total volume of sol and electrolyte 10 c. c. by the addition of the requisite amount of water.

Similar experiments were performed with $Fe(OH)_3$ sol using $K_2SO_4$ as the coagulating electrolyte.

*Determination of the Chemical and Physical Adsorption of the Precipitating Ion.*—$As_2S_3$ sol (500 c. c.) was taken and the requisite amount of *N*/20-$BaCl_2$ added just to coagulate the sol in an hour. The total volume of the sol and the electrolyte was always made up to 1000 c. c. with distilled water. This was allowed to stand for an hour, after which the sol was filtered off carefully, and the precipitating ion in the supernatant liquid was estimated. Barium was estimated as $BaSO_4$ in the case of $As_2S_3$ sol by the usual method.

Similarly in the case of $Fe(OH)_3$ sol, 100 c. c. of the sol in (A) and 250 c. c. in (B) were taken and the electrolyte necessary to coagulate in an hour was added as determined from the preliminary experiments. The total volume in (A) was made up to 200 c. c. and in (B) 500 c. c. with distilled water.

Again 500 c. c. of the $As_2S_3$ sol, and 100 c. c. of the $Fe(OH)_3$ sol in (A) and 250 c. c. in (B) were taken in different flasks. The $As_2S_3$ sol was coagulated by

HCl and the coagula washed till free from chlorine. The whole of the precipitate was suspended in 500 c. c. of distilled water and the same concentration of the $BaCl_2$ solution as was necessary for the coagulation of an equal amount of the sol, as done above, was added. Here also the total volume of the suspension and the electrolyte was made up to 1000 c. c. This was also kept for an hour and filtered. After this the estimations of the precipitating ions were carried out exactly in the same manner as in the case of the respective sols Similar experiments were done with $Fe(OH)_3$ sol using KCl for coagulation.

Further, the $As_2S_3$ sol was stabilised by the addition of (*a*) pure sucrose, (*b*) pure glucose, and (*c*) $H_2S$ solution of known concentration prepared in conductivity water. The ferric hydroxide sol was stabilised by the addition of dilute solution of known concentration of HCl.

In all these cases of the stabilised sols the amount of the "chemical adsorption" of the precipitating ion as well as the "physical adsorption" at the coagulating concentrations were determined exactly as stated above in presence of the added substances.

When $H_2S$ was added to $As_2S_3$ sol, it was stabilised as shown by the higher coagulating concentration of the added electrolyte. This stabilisation caused an increased adsorption of the Ba ions. There was not a marked increase in the "physical adsorption" of the precipitating ion but there was a considerable increase in the "chemical adsorption". Exactly comparable experiments were carried out without the addition of $H_2S$ solution.

Such experiments were also performed with $Fe(OH)_3$ sol by first stabilising it by the addition of dilute HCl of known concentration, and then determining the adsorption of the precipitating ion. Exactly comparable experiments were done without the addition of HCl solution.

*Determination of the Charge on each particle of* $As_2S_3$ *Sol and the Ferric Hydroxide Sol.*—The "chemical adsorption" was determined by subtracting the "physical adsorption" from the amount of the total adsorption of the precipitating ion. This gave the total amount of the charge in the given quantity of the sol. The number of the particles in the sol was determined by finding out the radius of the $As_2S_3$ sol, by extrapolating the results of Börjeson (*Kolloid Z.*, 1920, **18**, 27) who succeeded in determining the absolute size of the particle in a series of $As_2S_3$ sols obtained from $As_2O_3$ solutions of various concentrations. The density of the arsenious sulphide particles has been taken to be the same as in the bulk. From the mass of a single particle the number of the particles has been calculated in the amount of the colloid taken. Given the number of the particles and the total charge on them, the charge on each particle has been calculated by simple division. Detailed observations and calculations of a set of readings on $As_2S_3$ sol and $Fe(OH)_3$ sol are given in Tables I—III.

The charges at other concentrations and under different conditions of the respective sols have been similarly calculated and are given in Tables II and III.

TABLE I.

| | $As_2S_3$ sol, (500 c.c.) | Ferric Hydroxide sol. (100 c.c.) |
|---|---|---|
| Amount in the sol ... ... | 11·23g ($As_2S_3$) | 0·848 g $[FeOH]_3$ |
| Radius of the particles at above conc. .. | 75 μμ (by extrapolation) | 50 μμ |
| Vol. of each particle ... ... | $1·768 \times 10^{-16}$ c. c. | $5·24 \times 10^{-16}$ c.c. |
| Wt. of each particle ... | $6·277 \times 10^{-16}$ g. | $1·834 \times 10^{-15}$ g |
| Average density of the mass ... | 3·55 g. per c c. | 3·7 g. per c.c. |
| No. of the particles ... | **$1·789 \times 10^{15}$ | *$4·37 \times 10^{14}$ |
| Total adsorption of ions ... | **0·0339 g. (Ba) | *0·00533 g ($SO_4''$) |
| "Physical adsorption" of ions ... | **0·0049 g. ,, | *0 00047 g. ($SO_4$). |
| "Chemical adsorption" of ions ... | **0·0290 g. ,, | *0·00486 g. ($SO_4''$) |
| †Charge on each particle ... | $6·84 \times 2 \times 10^{-5}$ e.s.u. | $6·70 \times 10^{-5}$ e.s.u. |

†Calculated as :— $\frac{\text{Quantity of the charge in the amount of Ba or } SO_4'' \text{ chemically adsorbed}}{\text{Number of the particles in the amount of the sol taken}}$.

** Figures refer to 500 c. c. of the $As_2S_3$ sol.

* Figures refer to 100 c. c of $Fe(OH)_3$ sol.

## DISCUSSION

From the results given in Tables II and III, it is clear that the "chemical adsorption" of the precipitating ion increases when the sol is stabilised, (*i*) by the addition of an electrolyte such as $H_2S$ to $As_2S_3$ sol and HCl to $Fe(OH)_3$ sol, or (*ii*) the addition of carbohydrates such as sucrose and glucose to the $As_2S_3$ sol. Under identical conditions the "physical adsorption" does not change to an appreciable extent; if at all, it shows a slight tendency to increase in both the above cases. Hence the explanation of Weiser (*J. Phys. Chem.*, 1924, **28**, 1253) that the stabilisation is due to the cutting down of the adsorption of the precipitating ion by the adsorption of the non-electrolytes is not substantiated. Sen (*Kolloid Z.*, 1926, **38**, 310) has also reported an increase in the adsorption of the ions in presence of sugar.

The stability produced on adding minute traces of electrolytes to pure sols has been accepted by various observers as due to an adsorption of the similarly charged ions. Mukherjee (*loc. cit.*) is of opinion that in the case of pure sols an initial low electric charge on the colloid indicates a low amount of primary adsorbed ions and it shall favour more primary adsorption of the ions carrying the same charge as the colloid. This view is supported by the fact that stabilisation usually occurs on the addition of uni-univalent salts. This adsorption necessarily produces an increase in the charge and an increase in the "chemical adsorption" observed in this case can be easily explained.

## TABLE II.

### *Charge on arsenious sulphide sol.*

$As_2S_3$ sol taken = 500 c.c. Radius of the particle = 75μμ. Total vol. = 1000 c.c.

| Nature of sol. | $N/20$-$BaCl_2$ added. | Sol. conc. = 22·46 g./litre. No. of particles = $1·842 \times 10^{15}$. Sucrose and glucose, 50 g each. | | | | Sol conc. = 12 g./litre. No. of particles = $1·789 \times 10^{15}$. Sucrose and glucose, 75g. each. | | | | Sol. conc = 24·72 g./litre. No. of particles = $1·968 \times 10^{15}$. Sucrose and glucose, 150g. each. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Adsorption of Ba ions. | | | Charge in | Adsorption of Ba ions. | | | Charge in | Adsorption of Ba ions. | | | Charge in |
| | | Total. | Phys. | Chem. | e. s. u. | Total. | Phys. | Chem. | e. s. u. | Total. | Phys. | Chem. | e. s. u. |
| Pure sol ... | 50 c. c. | 0·0339 g. | 0·0049 g. | 0·0290 g. | $6·84 \times 10^{-5}$ | 0·0355 g. | 0·0053 g | 0·0302 g. | $6·91 \times 10^{-5}$ | 0·0374 g. | 0·0054 g. | 0·0320 g | $6·82 \times 10^{-5}$ |
| Sol + sucrose ... | 55 | 0·0394 | 0·0051 | 0·0343 | 8·09 | 0·0405 | 0·0055 | 0·0350 | 8·02 | 0·0434 | 0·0058 | 0·0376 | 8·05 |
| Sol + glucose ... | 55 | 0·0398 | 0·0052 | 0·0346 | 8·16 | 0·0411 | 0·0056 | 0·0355 | 8·13 | 0·0437 | 0·0058 | 0·0379 | 8·12 |
| Sol + $N/20$-$H_2S$ | | 0·0401 | 0·0052 | 0·0349 | 8·23 | 0·0415 | 0·0056 | 0·0359 | 8·24 | 0·0444 | 0·0059 | 0·0385 | 8·25 |
| | | with 20 c.c. of $N/20-H_2S$ | | | | with 30 c.c. of $N/20-H_2S$ | | | | with 50 c.c. of $N/20-H_2S$ | | | |

## TABLE III.

### *Charge on ferric hydroxide sol.*

Radius of the particle = 50 μμ

Sol. A taken = 100 c.c. Cl content = 0·84 g./litre. Total vol. = 200 c.c.

Sol A. (conc. 8·478g/litre) No. of particles = $4·37 \times 10^{14}$

| Nature of sol. | Adsorption of $SO_4''$ Total. | Phys. | Chem. | Charge in e.s.u. |
|---|---|---|---|---|
| | $N/20$-$K_2SO_4$ added = 5·00 c.c in 1 hr. | | | |
| Pure sol | 0·00533g. | 0·00047g. | 0·00486g. | $6·70 \times 10^{-5}$ |
| " | 0·00532 | 0·00047 | 0·00485 | 6·67 |
| " | 0·00534 | 0·00048 | 0·00486 | 6·70 |
| | $N$-$K_2SO_4$ added = 6·00 c.c. in 1 hr. | | | |
| Sol + 2 c.c. of $N/10$-HCl | 0·00670 | 0·00052 | 0·00618 | 8·52 |
| " | 0·00671 | 0·00052 | 0·00619 | 8·54 |
| " | 0·00670 | 0·00056 | 0·00614 | 8·47 |

Sol. B taken = 250 c.c.
Cl content = 0·68 g./litre. Total vol. = 500 c.c.

Sol B. (conc. 7·749g /litte) No. of particles = $9·993 \times 10^{14}$.

| Nature of sol. | Adsorption of $SO_4''$ Total. | Phys | Chem. | Charge in e s u. |
|---|---|---|---|---|
| | $N/20.K_2SO_4$ added = 12·5c.c. in 1 hr. | | | |
| Pure sol | 0·0124g. | 0·0016g. | 0·0108g. | $6·52 \times 10^{-5}$ |
| " | 0·0123 | 0·0017 | 0·0106 | 6·40 |
| " | 0·0125 | 0·0016 | 0·0109 | 6·58 |
| | $N/20$-$K_2SO_4$ added = 15·0 cc. in 1 hr. | | | |
| Sol + 5 c.c. of $N/5$-HCl | 0·0156 | 0·0017 | 0·0139 | 8·39 |
| " | 0·0160 | 0·0017 | 0·0143 | 8·63 |
| " | 0·0152 | 0·0017 | 0·0135 | 8·15 |

But an increase in the "chemical adsorption" produced by the addition of non-electrolytes cannot be due to an increase in the charge on the particles on account of the adsorption of the similarly charged ions by them, because here no electrolyte is added. An actual increase in the value of the charge can take place by an increase in the dielectric constant or a decrease in the thickness of the double layer, according to the equation $e = VD/4\pi\delta$ provided the radius of the particle and the potential of the double layer remains the same. We agree with Mukherjee and co-workers (*J. Indian Chem. Soc.*, 1928, 5, 704) that the potential of the double layer is not determined by the change in the dielectric constant, as Freundlich had assumed, and further it appears to us that the change in the value of the charge *e*, cannot be wholly explained by the change in the dielectric constant alone. It is rather more probable that the thickness of the double layer alters.

In this connection it is of importance to note that Wo. Ostwald (*J. Phys. Chem.*, 1938, 42, 981) has pointed out that the "density of the charge instead of the magnitude of the charge" and the "compression of the double layer" might be responsible for the coagulation of a colloid; but certainly they are insufficient by themselves. Whether really an alteration in the thickness of the double layer is finally the cause of this increase in the concentration of the precipitating ion when the stabilisation is brought about by the addition of the non-electrolytes, further experiments can show. For the present it can only be taken as a suggestion.

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# PYRIDINE COMPLEX OF METALLIC PERCHLORATES. PART I.

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Pyridine compounds of the perchlorates of silver, copper (ic), magnesium, calcium, strontium, barium, cadmium, zinc, mercury(ic), manganese, nickel and cobalt have been prepared. Compositions and characteristics of these compounds have been described. It has been found that the same pyridine compound is formed whether anhydrous or hydrated perchlorates are employed. No relationship seems to exist between the size of the metal atom or its ion and the number of pyridine molecules it can co-ordinate.

A large number of complex compounds of pyridine with various inorganic salts have been described in literature.* Most of the earlier investigations were, however, concerned with the preparation and analytical compositions of the substances formed, and little attempts were made to determine the structure of the complex compounds. Davis and his co-workers (*J. Amer. Chem. Soc.*, 1930, 52, 4069 ; 1934, **56**, 1061 ; 1936, **58**, 2153 ; 1940, **62**, 1276) were the first to make a systematic study of the metal-pyridine compounds. They found that these compounds were true co-ordination complexes and showed that where the number of molecules of pyridine was greater than the co-ordination number of the metal, the extra pyridine molecules were merely adsorbed. They also determined the affinities with which $C_5H_5N$ molecules were linked in the compound from measurements of their dissociation pressures at different temperatures.

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* Jorgenssen. (*J. prakt. Chem*, 1884, *ii*. 33, 502). Veret (*compt. rend.*, 1892, **115**, 464; 1897, **124**, 1155). Klobb, *ibid.*, 1894, **118**, 1271; Reitzenstein, *Annalen*, 1874, 282, 267; *Z. anong. Chem.*, 1898, **18**, 253. Pesci (*Gazzetta*, 1895, 25, 432). Pincousshn (*Z. anorg. Chem.*, 1897, **14**, 385). Tombeck, (*Ann. chim, phys.*, 1900, 21, 433; 1901, 22, 113). Litterscheid, (*Arch. Pharm.*, 1901, 239, 336; 1902, **240**, 74). Grossmann (*Ber.*, 1904, **37**, 839). Pfeiffer and Pimmer (*Z. anorg. Chem.*, 1905, **48**, 98). Werner *etal.* (*Ber.*, 1908, **39**, 1538). Davis and Logan (*J. Amer. Chem. Soc.*, 1928, **50**, 2497). Werner, (*J. Chem. Soc.*, 1925, 2577). Zvyagintsev, *etal.* (*Bull, aeav, sci., U.S.S.R.*, 1937, No. 3, p. 1255).

An examination of the previous work of the metal-pyridine compounds indicates clearly the necessity of a thorough investigation of this class of compounds, mainly because of the divergent results obtained by different workers in the field. The present work has been therefore undertaken in order to inquire into the nature, conditions of formation, stability and other characteristics of these compounds and to investigate them from chemical as well as physical aspects. For this purpose it seemed desirable to make a systematic study of the complexes which formed with different metallic salts of the same acid, and salts of perchloric acid was selected chiefly for two reasons. In the first place, pyridine compounds of metal perchlorates are not known, and secondly, the ammines of perchlorates of coper, silver, zinc, cadmium, calcium, strontium, barium, nickel and cobalt have been fully investigated by Ephraim and his collaborators (*Ber.*, 1913, **46**, 3103 ; 1915, **48**, 638, 1770 ; *Helv. Chim. Acta*, 1934, **17**, 296) and the ammines of the perchlorates of the alkali and alkaline earth metals by Smeets (*Natur. Tijdschr.*, 1935, **17**, 83, 213 ; 1939, **21**, 149). As pyridine would replace ammonia, molecule for molecule, naturally parallelism between the ammonia-metal perchlorates and the pyridine compounds of the latter could be expected.

## EXPERIMENTAL

Perchlorates of Ag, $Cu^{II}$, Mg, Ca, Sr, Ba, Cd, Zn, Hg (ic), Mn (ous) Ni and Co were prepared by the action of 20g. of perchloric acid (A.R.) on freshly precipitated and carefully washed oxide or carbonate of the respective metal. The resulting solutions were filtered where necessary and the filtrate. on concentration, gave crystals of the perchlorates which were separated from the liquid by filtering through a Buchner funnel and washed with ice-cold water. The crystals were dissolved in a small quantity of distilled water and recrystallised. The purity of the product was confirmed by analysis. All the perchlorates except that of silver contained water of crystallisation, and their composition agreed with those stated by earlier workers (Serullas, *Ann. chim. phys.*, 1831, *ii*, **46** 297 ; Salvadori, *Gazzetta*, 1912, **42**, 458 ; Weinland and Ensgraber, *Z. anorg. Chem.*, 1914, **84**, 370 ; Willard and Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 286).

To prepare the pyridine compounds, 2 to 4 g. of the crystalline perchlorate were dissolved in 20 to 30 c.c. of specially purified and freshly distilled pyridine (b.p. 114·5°), the solution being effected by warming. The solution was then heated on a water-bath for a short time, and on cooling, beautiful crystals separated in every case. These were collected in a Gooch crucible, washed with a little cold pyridine, and freed from the latter by suction. The crystals were dried by pressing between folds of filter paper and transferred into a glass-stoppered weighing bottle for analysis.

For determination of pyridine in the case of the colourless compounds, a small quantity of the substance was directly weighed out into an Erlenmeyer flask, dissolved in a little water and titrated with *N*/10-hydrochloric acid solution, using methyl orange as indicator. For estimation of pyridine in the coloured compound, a modification of the method described by Lange (*Ber.*, 1883, 21, 579) was followed. From the aqueous solution of a weighed quantity of the coloured compound, made strongly alkaline with sodium hydroxide, the pyridine was steam-distilled into standard *N*-sulphuric acid solution, and the excess of acid was then titrated back with *N*/2-sodium hydroxide solution. Blank experiments with weighed amounts of purified pyridine showed that the method is accurate to about 1% only, mainly on account of the fact that a sharp end-point is not obtained. Other indicators, such as methyl red, congo red, etc., were tried, but methyl orange gave the best results.

For determination of the metals, the solutions left after titration of pyridine in the case of the colourless compounds or those left in the round-bottomed flask after steam distillation in the case of the coloured compounds, were used. In many cases, estimation of the metals was also made directly with weighed quantities of pyridine compound, and the values obtained agreed well with those given after the removal of pyridine except in the cases of copper and cobalt where it was found that the presence of pyridine prevented complete deposition of the metals. Pyridine must also be previously removed for direct conversion of the pyridine compounds into sulphates by heating with concentrated sulphuric acid, otherwise decomposition takes place with explosion.

The composition of the compounds obtained with a short description of their properties and the analytical results are given below.

| Compounds. | Properties. | Results of analysis. Calc. | | Found. | |
|---|---|---|---|---|---|
| | | Metal. | Pyridine. | Metal. | Pyridine. |
| $AgClO_4 \cdot 4C_5H_5N$ | Colourless cubic crystals. Fairly stable. | 20·59% | 60·41% | 20·1; 20·5% | 60·1; 59·9% |
| $Cu(ClO_4)_2 \cdot 4C_5H_5N$ | Small violet-blue crystals. Stable. Not hygroscopic. | 10·98 | 54·66 | 10·8; 10·9 | 54·9; 55·5 |
| $Mg(ClO_4)_2 \cdot 6C_5H_5N$ | Colourless crystals. Extremely hygroscopic. | 3·49 | 68·01 | 3·4; 3·3 | 67·6; 67·4 |
| $Ca(ClO_4)_2 \cdot 6C_5H_5N$ | Colourless crystals. Highly deliquescent in moist air Unstable. | 5·63 | 67·91 | 5·5; 5·4 | 66·0; 67·2 |
| $Sr(ClO_4)_2 \cdot 6C_5H_5N$ | Ditto. | 11·52 | 62·35 | 11·4; 11·3 | 62·7; 62·2 |
| $Ba(ClO_4)_2 \cdot 6C_5H_5N$ | Colourless crystals. Deliquescent, but less so and more stable than Ca and Sr compounds. | 16·96 | 58·54 | 17·5; 17·3 | 57·5; 58·1 |
| $Zn(ClO_4)_2 \cdot 4C_5H_5N$ | Colourless hexagonal pyramids. Fairly stable. Not hygroscopic. | 11·27 | 54·46 | 11·2; 11·3 | 54·4; 54·8 |
| $Cd(ClO_4)_2 \cdot 6C_5H_5N$ | Stable colourless crystals. Not deliquescent. | 14·30 | 60·39 | 14·6; 14·2 | 59·9; 59·2 |
| $Hg(ClO_4)_2 \cdot 6C_5H_5N$ | Colourless crystals. Not hygroscopic. Quite stable. | 22·95 | 54·29 | 22·9; 22·6 | 54·5; 53·7 |
| $Mn(ClO_4)_2 \cdot 8C_5H_5N$ | Lilac crystals. Not deliquescent. Partially hydrolysed with water. | 6·20 | 71·36 | 6·0; 6·1 | 71·5; 71·6 |
| $Ni(ClO_4)_2 \cdot 6C_5H_5N$ | Pale green crystals. Stable. Not very hygroscopic. | 8·04 | 64·82 | 8·3; 8·2 | 64·6; 64·7 |
| $Co(ClO_4)_2 \cdot 6C_5H_5N$ | Pink haxagonal prisms. Soluble in chloroform. Fairly stable. | 8·05 | 64·81 | 8·1; 8·2 | 64·7; 64·9 |

It will be seen that the compounds of the alkaline earth metals and that of magnesium are extremely hygroscopic. They deliquesce so rapidly in moist air that it is almost impossible to separate them from pyridine during rainy season. When kept in a desiccator over sulphuric acid, all these pyridine compounds lose pyridine more or less rapidly. They, however take up pyridine when exposed to pyridine vapour and return to their original composition. It seems that these pyridine complexes are not interstitial compounds, because the crystalline form of the pyridine complex as well as its solubility in pyridine differs entirely from the corresponding perchlorate. The hydrated perchlorates generally form needle-like crystals, while the pyridine compounds assume various crystalline forms. For example, while $AgClO_4$ crystallises as long needles, $AgClO_4 \cdot 4C_5H_5N$ crystallises in the form of cubes, and while $Co(ClO_4)_2 \cdot 6C_5H_5N$ comes out as hexagonal prisms, $Co(ClO_4)_2 \cdot 6H_2O$ forms needle-shaped crystals. The solubility of the perchlorate and its corresponding pyridine compound in water is also different.

It has been found that the water of crystallisation of the perchlorates has no influence on the formation of the pyridine compound. About 6 g. of needle-like crystals of hydrated magnesium perchlorate were heated first at 120° when about 30% of the water of crystallisation were lost, and then the temperature was gradually raised to 230-250° until there was no further loss of water. The total loss of water amounted to 32·67%, while the theoretical value for the hexahydrate is 32·62%. The white anhydrous material thus obtained was taken out of the crucible while still hot, ground to powder and kept in a vacuum desiccator over concentrated sulphuric acid. The pyridine compound obtained by dissolving this anhydrous magnesium perchlorate had the same crystalline form and the same analytical composition as that given by $Mg(ClO_4)_2 \cdot 6H_2O$. Similarly when some crystals of barium perchlorate were heated to constant weight at 250°, they lost all water. The total loss of water amounted to 13·79%, while the calculated value for $Ba(ClO_4)_2 \cdot 3H_2O$ is 13·85%. The anhydrous barium perchlorate also gave the same pyridine compound as the hydrated crystals.

## DISCUSSION

As all these pyridine compounds separated from pyridine solutions, they must represent the highest possible pyridinated complexes. It will be seen from the table that the perchlorates of silver, copper and zinc can take up only 4 molecules of pyridine each, the perchlorares of magnesium, calcium, strontium, barium, cadmium, mercury, nickel and cobalt 6 molecules of pyridine each, and manganese as many as 8 molecules of pyridine. In discussing the ammoniated compounds of metallic perchlorates, Ephraim (*Ber*, 1912, 45, 1323) stated that those metals whose atomic volume is less than 14 can take up 6 molecules of ammonia, but those metals whose atomic volumes are greater than this number cannot form stable hexammines. Those in which the atomic volumes are very large (Ba, Sr, Ca) give ammines of a different class ; these decompose readily with liberation of much ammonia and with no pause at the hexammine stage. As both ammonia and pyridine are co-ordinated to the metal atom through the nitrogen atom, it was expected that pyridine compounds would behave in the same manner as the ammonia compounds. From an examination of the pyridine compounds described in the present paper, there appears to be no relationship between the number of molecules of pyridine which can be co-ordinated and the size of the metal atom or its ion. For instance, although copper and manganese have almost the same atomic volumes, only 4 molecules of pyridine can attach themselves to copper, but manganese can take up double this number. In fact, similar anomalous behaviour is also observed when the ammines of metallic perchlorates are compared. When the ammoniated compounds of the perchlorates are examined, it is found that the highest ammine of zinc has the formula $Zn(ClO_4)_2 \cdot 6NH_3$ (Ephraim, and Zapata, *Helv. Chim. Acta*, 1934, **17**, 296) and that of silver has the formula $AgClO_4 \cdot 3NH_3$ although the sizes of the metal atoms or their ions do not justify that the former should take up twice the number of $NH_3$ molecules as the latter. It appears therefore that the co-ordination number does not depend merely on the size of the co-ordinating metal atom or its ion but rather on the capacity of expansion of its electronic orbits so that it may be possible to accommodate all the electrons necessary to form the co-ordinate links. In recent years a considerable amount of research has centred round the determination of the structure of co-ordination compounds with all the powerful physical methods at the disposal of the modern chemist and old observations furnished in the light of the present-day knowledge, but it has not yet been possible to discover the factors which determine the co-ordination number of elements. There is increasing evidence in favour of the view that co-ordinate links and principal valencies are closely connected, and it seems, that it is neccssasy to determine the structure of co-ordination compounds as a whole and not of the central metal atom only.

Measurements of lowering of the freezing point and elevation of the boiling point, conductivity and dissociation pressures are in progress.

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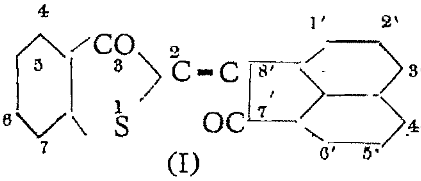
# DYES DERIVED FROM ACENAPHTHENEQUINONE. PART VIII. (7-METHYL)THIONAPHTHENE-ACENAPHTHYLENE-INDIGOS

By Sisir Kumar Guha

Acenaphthenequinone and its various substituted products have been condensed with 7-methyl-3-hydroxythionaphthene and the corresponding thioindigoid vat dyes obtained. The previous method of preparation of 7-methyl-3-hydroxythionaphthene has been modified. 7 : 7′-Dimethylthioindigo has been obtained from 7-methyl-3-hydroxythionaphthene

In previous parts of this series (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 682 ; 1936, **13**, 94 ; 1938, **15**, 23) the influence of a methyl group in the 4-, 5-, and 6-position of the thionaphthene nucleus of 2-thionaphthene-acenaphthylene-indigo (I) was fully studied, and the variation of colour in relation to the constitution of these three classes of dyes was also established, both qualitatively and quantitatively.



(I)

With a view to completing this series, the study of the influence of a Me group in the 7-position of the thionaphthene nucleus of (I) was undertaken, and for this purpose acenaphthenequinone and its derivatives were condensed with 7-methyl-3-hydroxythionaphthene (Guha, *J. Indian Chem. Soc.*, 1939, **16**, 219)

The 7-methylthionaphthene-acenaphthylene-indigos are beautiful, red and deep red crystalline products. They develop lustre when rubbed vigorously, analogous to the 4-, 5- and 6-methyl dyes (Guha, *loc. cit.*).

The dyeing shades have been fully developed in all cases on wool from an acid bath (*cf. J. Indian Chem. Soc.*, 1933, **10**, 680) and also on cotton from the hydrosulphite vat, except the methoxy derivative which offered resistance to reduction in the vat in the same manner as the methoxy compounds belonging to the 4-, 5- and 6-methyl series, 5-chloro series, and 2 : 3-naphthathiophene series (Guha, *loc. cit. J. Indian Chem. Soc.*, 1937, **14**, 710 ; 1939, **16**, 127).

The preparation of 7-methyl-3-hydroxythionaphthene required modification as the vigorous reaction which had occurred resulted in a poor yield. The method adopted now not only increased the yield, but also gave a purer product more easily. The cause of the low melting point of the product by the previous method was found to be due to absorption of oily mother-liquor. By the oxidation of 7-methyl-3-hydroxythionaphthene, 7 : 7′-dimethylthioindigo (*cf.* D. R. P. 241910) was obtained for the purpose of comparing its dyeing properties with those of the three isomeric dimethylthioindigos and their parent compound (Guha, *J. Indian Chem. Soc.*, 1938, **15**, 506).

The quantitative measurement of the depth of colour of these 7-methyl dyes (absorption curves, absorption maxima, etc.) and a discussion of the result of the comparative study of all the isomeric methylthionaphthene-acenaphthylene-indigos considered together, as well as of the dimethylthioindigos, will be communicated in a succeeding paper.

## EXPERIMENTAL

2-(7-*Methyl*)-*thionaphthene-acenaphthylene-indigo.*—When a solution of acenaphthenequinone (0·546g.) and 7-methyl-3-hydroxythionaphthene (0''492g ) in boiling glacial acetic acid (40 c c.) was treated with concentrated hydrochloric acid (4 c.c.), a thick red crystalline mass separated. Mote glacial acetic acid (40 c.c.) was added and the mixture shaken well and boiled for 20 minutes. The sharp needle-shaped red product (0·825g.) was finally crystallised from glacial acetic acid, m.p. 304°. Separated from alcohol, it was yellowish red in colour. It dyes cotton dark red from a violet-blue hydrosulphite vat, and wool a similar shade from an acid bath. (Found : S, 9·92. $C_{21}H_{12}O_2S$ requires S, 9·75 per cent).

2-(7-*Methyl*)-*thionaphthene*-8'-(3'-*chloro*)*acenaphthylene-indigo* was similarly prepared from 3-chloroacenaphthenequinone (0·6495g.). and 7-methyl-3-hydroxythionaphthene (0·492g.) dissolved in boiling glacial acetic acid (60 c.c.) and conentrated hydrochloric acid (3 c.c.). The thick mass of the thread-like, yellowish red needles was treated with 30 c.c. more of glacial acetic acid and boiled for 20-25 minutes, filtered and collected. The dye (0·907g.) was crystallised from glacial acetic acid in fine red needles, m. p. 274°. It dyes cotton red from a blue hydrosulphite vat, and wool yellowish red from an acid bath. (Found : Cl, 10·27. $C_{21}H_{11}O_2ClS$ requires Cl, 9·79 per cent).

2-(7-*Methyl*)-*thionaphthene*-8'-(3'-*bromo*)*acenaphthylene-indigo* separated from a red solution of 3-bromoacenaphthenequinone (0·6525g.) and 7-methyl-3-hydroxythionaphthene (0·41g.) in 80 c.c. of boiling glacial acetic acid and 3 c.c. of concentrated hydrochloric acid on heating for 20 minutes. The thread-like deep red needle-shaped substance (0 821g.) was crystallised from a large quantity of acetic acid in long fine needles, m. p. 264-65°. It dyes cotton the same shade as the chlorocompound and wool red from an acid bath. (Found : Br, 19·54. $C_{21}H_{11}O_2BrS$ requires Br, 19·65 per cent).

2-(7-*Methyl*)-*thionaphthene*-8'-(1'-*methoxy*)-*acenaphthylene-indigo.*—The red-brown solution obtained by dissolving $\beta$-methoxyacenaphthenequinone (0·636g.) and 7-methyl-3-hydroxythionaphthene (·0492g) in 85 c.c. of boiling glacial acetic acid, when treated with concentrated hydrochloric acid (4c.c ), turned deep red (almost black). After a short while a scarlet-red precipitate separated which was boiled for 25 minutes and collected. The dye (0·444g.) was crystallised from pyridine in fine clusters of needle, m. p. 300°. It dyes cotton a faint pink shade from a bluish violet vat, and wool red from an acid bath. (Found : S, 9·1. $C_{22}H_{14}O_3S$ requires S, 8·93 per cent).

7-*Methyl*-3-*hydroxythionaphthene.*—A solution of *o*-methylphenylthioglycollic acid (10g.), m.p. 108° (*cf.* Rabaut, *Bull. Soc. Chim..* 1902, *iii*, 27, 690) records m.p. 106°) in hot, dry benzene (120-130 c.c.) was treated gradually with phosphorus pentoxide (40 g.). It was boiled on the water-bath for ½ hour, and left at room temperature for 48 hours. After removing benzene, the bulky blackish brown soft residue was dissolved in ice-cold aqueous alkali; the solution acidified with dilute hydrochloric acid and distilled in steam. The distillate containing the colourless crystalline substance was left overnight in a cooled chamber ; filtered, washed with a little cold water, and dried in a vacuum desiccator, when it turned faint pink, yield about 2 g. It was crystallised from petroleum ether in long rectangular plates, m.p. 80-81°. (Found : S, 19·37. $C_9H_8OS$ requires S, 19·51 per cent)

7 : 7′-*Dimethylthioindigo-7-methyl-3-hydroxythionaphthene* was dissolved in the required quantity of warm dilute sodium hydroxide (2*N*). An aqueous solution of potassium ferricyanide (5%) was added gradually with shaking until a red precipitate was no longer formed and the solution warmed for ½ hour on the water-bath. The precipitate was collected, washed well with hot water and dried. The dye was crystallised from nitrobenzene in fine dark red needles, not melting below 318°. It is soluble in pyridine, nitrobenzene, aniline, xylene, chloroform ; difficultly soluble in benzene and carbon tetrachloride ; sparingly soluble in acetic acid and alcohol The solution of the substance in concentrated sulphuric acid is deep green ; water precipitates the original substance. It dyes cotton a pleasant violet-red from a light greenish yellow hydrosulphite vat, and wool dark violet-red colour from an acid bath. (Found : S, 20·13. $C_{18}H_{12}O_2S_2$ requires S, 19·75 per cent).

The author's thanks are due to Principal K. Prosad, I.E.S., and Dr. R. C. Roy, D.Sc. for their interest during the progress of the work.

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# VISCOSITY OF MIXED SOLUTIONS CONTAINING THREE AND FOUR IONIC SPECIES

By Amritansu Sekhar Chakravarti

Viscosity of two binary electrolyte mixtures with common cations and two without common ions (each in three different proportions) as well as the viscosity values for solutions of three simple electrolytes are reported. Onsager and Fuoss' limiting law for mixed ionic solutions has been established in these cases and an equation of the Jones and Dole type applied to the results. The coefficient of the square root term '*A*' has been shown to be a linear function of composition. The same is true of the coefficient of the linear term '*B*', except in the case of NaCl-BaCl$_2$ mixtures, whose results are taken from a previous paper. The additive principle is not applicable to the viscosity of a mixed solution of two electrolytes, the observed values being systematically too low.

The variation in viscosity with concentration of solutions containing more than two kinds of ions has been worked out mathematically by Onsager and Fuoss (*J. Phys. Chem*, 1932, 36, 2689). The viscosity variation of solutions containing two salts was studied experimentally by Chakravarti and Prasad (*Trans. Faraday Soc.*, 1940, **36**, 557). The present work is an extension of the same. The pairs examined will be evident from the tables. In these studies in any particular set, the ratio of the concentrations of two salts was fixed and change in viscosity was noted with change in total molecular concentration.

## EXPERIMENTAL

The experimental technique and procedure have been described in a previous communication (*J. Indian Chem. Soc.*, 1938, **15**, 301). The viscometer used had a capillary of 10 cm. length, 0·028 cm. diameter with an upper bulb of 5 c.c. capacity. The approximate time of efflux for water was 29 mins. No kinetic energy or surface tension correction was considered necessary. Three readings for the time of flow were taken with a Venner time switch, graduated in tenths of seconds, agreeing with one another within 0·2 second. The time for water was determined before and after each solution. The pyknometers used were of about 64 and 55 c.c. capacity. Double distilled water was used in all the experiments. The thermostat was maintained at 35°±0·005. The error in viscosity measurements is expected to be less than 3 parts in 10,000.

Chemicals used were of the highest possible quality. Standard solutions of the dry single salts were prepared and their strength verified gravimetrically. Mixtures having the two salts in any proportion were prepared by mixing the required volume of the two standard solutions. Mixtures were then diluted to decrease the total concentration to the required level.

In the case of single salt solutions as well as of all mixed solutions in which the proportion of the two salts were fixed, $\frac{\eta/\eta_0 - 1}{\sqrt{c}}$ plotted against $\sqrt{c}$ gave straight lines, which means that mixture of two salts, if their proportion is fixed, behaves like single salts. Thus for all these cases the equation

$$\frac{\eta}{\eta_0}=1+A\sqrt{c}+Bc$$

holds good. In this equation $\eta/\eta_0$ is the relative (with respect to water at the same temperature) viscosity of the solution corresponding to the total concentration, $c$ *i.e.* $(c_1+c_2)$ in g. moles per litre and '$A$' and '$B$' are constants. As expected, the equation is not applicable in some cases up to the highest concentrations measured.

In the following tables (I and II) $\eta/\eta_0$ (obs.) stands for observed relative viscosity and $\eta/\eta_0$ (calc.) for the relative viscosity calculated from an equation of the type shown above.

### TABLE I.

| Comp. of the solute. | $A\times10^3$. | $B\times10^2$. | $\left[\frac{\eta}{\eta_0}\text{(obs.)}-\frac{\eta}{\eta_0}\text{(calc.)}\right]\times10^4$ corresponding to conc. 0·01. | 0·02. | 0·03. | 0·04. | 0·05. | 0·06. | 0·07. | 0·09. | 0·12. | 0·16. | 0·20. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pure $K_2SO_4$ | 20 | 17·0 | −3 | −3 | +2 | +1 | +2 | 0 | +0 | — | — | — | — |
| Pure KCl | 8 | 0·0 | 0 | −1 | 0 | +4 | −1 | 0 | −3 | — | — | — | — |
| Pure $NaNO_3$ | 7 | 6·0 | 0 | 0 | −1 | +1 | +0 | +1 | +1 | — | — | — | — |
| $[K_2SO_4]:[KCl]=3:1$ | 17 | 12·0 | −3 | −3 | −2 | 0 | +2 | +2 | +2 | — | — | — | — |
| $[K_2SO_4]:[KCl]=1:1$ | 14 | 8·0 | −3 | +2 | +1 | 0 | +1 | +2 | +2 | — | — | — | — |
| $[K_2SO_4]:[KCl]=1:3$ | 11 | 4·0 | −1 | −1 | 0 | −1 | 0 | +2 | +3 | — | — | — | — |
| $[NaNO_3]:[NaCl]=3:1$ | 7 | 7·0 | +3 | +3 | 0 | +1 | −2 | −2 | −2 | −12 | −11 | −13 | −13 |
| $[NaNO_3]:[NaCl]=1:1$ | 7 | 8·0 | 0 | −2 | −2 | 0 | −2 | 0 | −1 | −6 | −7 | −6 | −11 |
| $[NaNO_3]:[NaCl]=1:3$ | 5 | 8·75 | +2 | 0 | +2 | −1 | −2 | −3 | −1 | −2 | −7 | −5 | −8 |

### TABLE II.

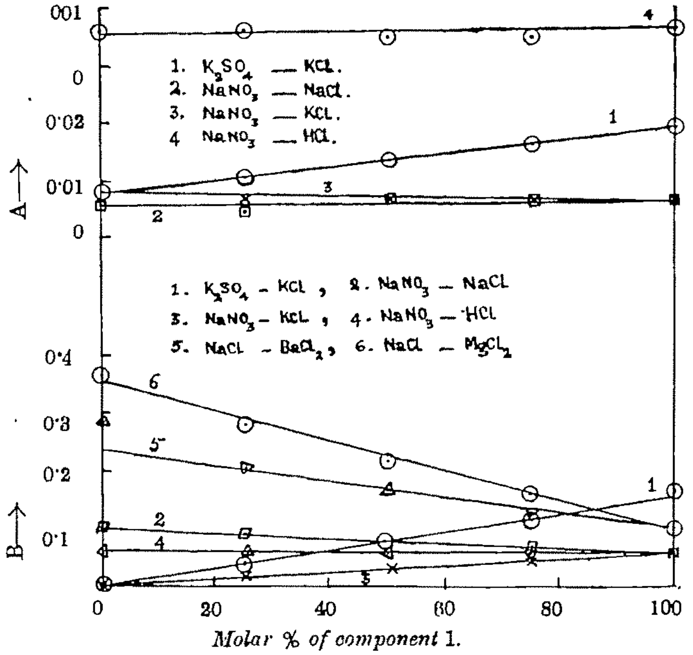
| Comp. of the solute. | $A\times10^3$. | $B\times10^2$. | $\left[\frac{\eta}{\eta_0}\text{(obs)}-\frac{\eta}{\eta_0}\text{(calc.)}\right]\times10^4$ corresponding to conc.: 0·01, | 0·02, | 0·03 | 0·04, | 0·05. | 0·07. | 0·10. | 0·15. | 0·20. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $[NaNO_3]:[KCl]=3:1$ | 7 | 4·2 | +1 | −1 | −3 | 0 | 0 | 0 | 0 | 0 | 0 |
| $[NaNO_3]:[KCl]=1:1$ | 7 | 3·1 | −2 | 0 | −1 | 0 | −1 | 0 | +3 | +1 | +3 |
| $[NaNO_3]:[KCl]=1:3$ | 7 | 1·5 | −2 | 0 | −1 | 0 | −1 | 0 | +1 | −1 | −3 |
| $[NaNO_3]:[HCl]=3:1$ | 5 | 5·8 | −3 | −4 | −3 | −2 | 0 | −2 | +1 | +1 | 0 |
| $[NaNO_3]:[HCl]=1:1$ | 5 | 5·8 | −3 | −3 | −1 | 0 | −1 | −1 | +1 | +5 | +7 |
| $[NaNO_3]:[HCl]=1:3$ | 6 | 6·0 | −3 | −3 | −2 | 0 | −3 | −2 | −1 | +2 | +2 |

The observed value at any concentration corresponding to any proportion of the salts for which the experiment has been done, can be easily found out. The viscosity of a solution of $NaNO_3$ and HCl in equimolecular proportion having a total concentration of 0·05 can be calculated from the equation,

$$\frac{\eta}{\eta_0}=1+A\sqrt{c}+Bc \quad \text{or} \quad \frac{\eta}{\eta_0}=1+5\times10^{3}\sqrt{0{\cdot}05}+5{\cdot}8\times10^{-2}\times0{\cdot}05=1{\cdot}0040.$$

Since the difference between the $\frac{\eta}{\eta_0}$ (obs.) and $\frac{\eta}{\eta_0}$ (calc.) $=-1\times10^{-4}$, the observed value of $\frac{\eta}{\eta_0}=1{\cdot}0039$.

The examination of the tables shows that for any salt pair, the values of $A$ and $B$ go on changing with the proportion of one of them. In the figure both $A$ and $B$ have been plotted against molar percentage composition $\left(\frac{c_1}{c_1+c_2}\times100\right)$ of one of the solutes. It is evident from the plot that $A$ is a linear function in molar percentage composition in all cases. The plots for $B$ also show a similar linearity except in the case of pure $BaCl_2$ in NaCl-$BaCl_2$ mixture. Some of the data for these plots have been taken from Chakravarti and Prasad's paper (*loc. cit.*).



The next question is whether the increase in viscosity due to two solutes can be considered to be additive, or not. If the increase was simply additive then the viscosity of a solution having a concentration of $c_1$ with respect to salt No. 1 and $c_2$ with respect to salt No. 2 would be given by the equation,

$$\frac{\eta}{\eta_0}=1+A_1\sqrt{c_1}+A_2\sqrt{c_2}+B_1c_1+B_2c_2.$$

Actually it is given by the equation,

$$\frac{\eta}{\eta_0}=1+A\sqrt{c_1+c_2}+B\,(c_1+c_2),$$

where $A - A_1 \cdot \frac{c_1}{c_1+c_2} + A_2 \frac{c_2}{c_1+c_2}$ and $B = \frac{B_1 c_1}{c_1+c_2} + \frac{B_2 c_2}{c_1+c_2}$, because both $A$ and $B$ are linear in composition of the solute ($B$ is not linear in NaCl-$BaCl_2$ mixtures).

This is enough to show that the increase is not additive. The following table will make it clearer. $\frac{\eta}{\eta_0}$ ($a$) means the viscosity calculated according to simple additive principle. $\frac{\eta}{\eta_0}$ (calc.) means the relative viscosity calculated in previous tables.

TABLE III.

$\left[\frac{\eta}{\eta_0}\text{(obs)} - \frac{\eta}{\eta_0}\text{(calc)}\right] \times 10^4$ are shown outside paranthesis and $\left[\frac{\eta}{\eta_0}\text{(obs)} - \frac{\eta}{\eta_0}(a)\right] \times 10^4$ in paranthesis.

| Comp. of the solute. | $c$=0·01. | 0·02. | 0 03. | 0 04. | 0·05. | 0·06. | 0·07. |
|---|---|---|---|---|---|---|---|
| [NaCl]:[$BaCl_2$]=3:1 | −2(−9) | 0(−10) | 0(−13) | +3(−14) | 0(−20) | 0(−23) | −1(−27) |
| [NaCl]:[$MgCl_2$]=4:1 | +1(−1) | 0(− 4) | +1(− 1) | −1(−6) | −1(−5) | +1(−3) | 0(−3) |
| [$K_2SO_4$]:[KCl]=3:1 | −3(−8) | −3(−11) | −2(−12) | 0(−12) | +2(−12) | +2(−13) | +2(−15) |
| [$K_2SO_4$]:[NaCl]=1:3 | −1(−7) | −1(−10) | 0(−11) | −1(−14) | 0(−16) | +2(−16) | +3(−14) |
| [$NaNO_3$]:[NaCl]=3:1 | +3( 0) | +3(0) | 0(− 5) | +1(−3) | −2(−8) | −2(−7) | −2(−8) |

The maximum experimental error in relative measurements is $3 \times 10^{-4}$. So it is evident that the observed viscosity is distinctly lower than that demanded by the additivity principle in most solutions. The difference goes on increasing as concentration increases. This has its parallel in the transference numbers (Wagner and Kuchler, *Physikal. Z.*, 1929, **30**, 623; Longworth, *J. Amer. Chem. Soc.*, 1930, **52**, 1897) and specific conductivity (Bray and Hurt, *J. Amer. Chem. Soc.*, 1911, **33**, 781).

It seems that Asmus (*Ann. Physik*, 1939, Sept. pp, 166-182) working on $CuSO_4-H_2SO_4$ mixture has come more or less to similar results as ours. On account of the continuance of the war the author has not been able to see the paper in original.

The author is grateful to Prof. B. Prasad for his kind help and guidance in this piece of work and to the Government of Orissa for the award of a research scholarship which enabled this work to be done.

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# THE COMPONENT GLYCERIDES OF VEGETABLE FATTY OILS. PART II. SAFFLOWER OIL.

By N. L. Vidyarthi

The safflower seeds (*Carthamus tinctorious*) yield 30·5% of oil which contains myristic acid (along with lauric and other lower acids) 1·5%, palmitic acid (3%), stearic acid (1%), archidic acid with a trace of lignoceric acid (0·5%), oleic acid (33%), linolic acid with a trace of linolenic acid (61%).

The glycerides have been determined by the bromination of the neutral oil and the component glycerides have been found to be myristo-oleolinolin (2%), myristodilinolin (1%), palmito-oleolinolin (7%), palmitodilinolin (4%), stearo-oleolinolin (2%), stearo dilinolin (1%), dioleolinolin (15%), oleo dilinolin (63%) and trilinolin (3%). The myristo glycerides contain a little of lauric and other lower acids, stearo glycerides contain little of archidic and lignoceric acid and the trilinolin contains traces of linolenic acid.

*Carthamus tinctorius*, Linn., commonly known as safflower (N.O. Compositæ) or Bastard saffron, is cultivated all over India both for oil seed as well as for the dye which is obtained from the flower. There was a time when safflower was considered to be an exceedingly important crop, but with the advent of the aniline dyes the area under cultivation of this crop has shrunk considerably during recent years. The seeds yield about 30% of oil, light pale in colour, which has been found to possess a very good drying property and is considered to be suitable for use in the manufacture of paints, varnish, linoleum etc. [ Rabak, *Oil Paint & Drug Reptr.*, 1927, III, No. 583 ]. A valuable property of this oil is its ability to prevent "after-yellowing" of white or pale tinted paints.

A good deal of work has been done in America and Germany on the composition of the fatty acids of safflower oils of these countries but the only work on the Indian safflower oils appears to have been done by Howard and Remington (*Bull. Agric. Res. Inst. Pusa*, 1921, No. 124, 14), who examined the physical and chemical characteristics of 24 samples of seeds. No work has been done as yet on the composition of the glycerides present in this oil. In general, the composition of fats and fatty oils varies according to the environment under which the seeds are grown. Ivanov, who has studied the effect of climate upon the composition of vegetable fats for a considerable period of years, with particular reference to the drying oils, has formulated (*Chem. Umchau*, 1929, **36**, 40) that the climate of southern lands favours the formation of oleic acid, whereas that of northern lands favours the formation of linoleic acids. The investigations have indicated that the flax seed and soyabeans, grown in temperate climates, have higher iodine values than those grown in the tropics. On the basis of this finding the composition of the safflower oil, grown in India, must have a different composition than those grown in America, Germany, Spain and other temperate climates. The present work was taken up with a view to finding out the composition of the fatty acids and the component glycerides of Indian safflower oil as no previous work has been recorded in literature. The methods adopted are similar as those for the determination of the component glycerides of Niger seed oil by Vidyarthi and Mallya (*J. Indian Chem. Soc.*, 1940, **17**, 87).

The oil has been found to consist of myristic, lauric and other lower acids 1·5%, palmitic acid 3·0%, stearic acid 1%, archidic and lignoceric acid 5%, oleic acid 35% and linoleic acid 61% and linolenic acido ·1% and the component glycerides have been found to be oleo-myristolinolin 3%, palmito-oleolinolin 7%, oleo-stearolinolin 2%, myristodilinolin 1·0% palmitodilinolin 4%, stearodilinolin 1%, dioleolinolin 15%, oleodilinolin 64% and trilinolin 3%.

The composition of safflower seems to be like that of the niger seeds which belong to the same botanical order. Safflower oil contains higher percentage of linoleic acid and lower of saturated and oleic acids and therefore according to the rules of even distribution dilinoleo glycerides are more than those found in the niger eed oil. Although there is no linolenic acid, the higher percentage of fully unsaturated glycerides accounts for the quick drying property of this oil.

## EXPERIMENTAL

The seeds were crushed and the husks were removed as far as possible. The husked seeds were extracted with carbon tetrachloride. The seeds contained 30·5% of oil having the following physical and chemical characteristics.

TABLE I.

| | | | |
|---|---|---|---|
| Sp. gravity at 27° | 0·9242 | Acid value | 6 3 |
| Refractive index at 27° | 1·4742 | Non saponifiables | 1·3 |
| Saponification value | 192·0 | Acetyl value | 13·2 |
| Iodine value (Wijjs) | 136·2 | Hexa bromide value | 0·2%. |

450 G. of the oil were saponified. The soap was mixed with sand and dried till it was friable, after which it was extracted with acetone. The solvent was distilled off from the extract and the residue was taken up in water and extracted with ether. The ethereal solution was washed free from soap with water. The water solution was mixed with the main bulk of soap and the fatty acids were liberated by treatment with dilute sulphuric acid. The mixed acids were subjected to the usual procedure of lead salt, alcohol and ether separation. The resulting fractions were converted into methyl esters and fractionally distilled under a reduced pressure of 0·2 mm

TABLE II.

| Materials. | Wt. | Percentage. | Sapon. equiv. | Iodine value. | Materials. | Wt. | Precentage. | Sapno. equiv | Iodine value. |
|---|---|---|---|---|---|---|---|---|---|
| Oil | 450 g. | ... | 291·5 | 136 | S. Solid acids | 25·1 g. | 6·1 | 268 6 | 34·3 |
| Mixed acids | 410·2 | 91·4 | 280·4 | 138 | Methyl ester of A. | ... | ... | 294·2 | 145·2 |
| A. Acid from the lead salts soluble in alcohol | 210·4 | 51·3 | 281·0 | 148 | ,, E. | ... | ... | 299·6 | 143·4 |
| | | | | | ,, S. | ... | ... | 282·1 | 33·8 |
| E. Acids from the lead salts soluble in ether | 174·6 | 42·6 | 286·2 | 144·6 | | | | | |

TABLE III.

*Fractionation of ester* A.

| | Fractions. | B p. | Wt. | Sapon. equiv. | Iodine value. | Fractions. | B p. | Wt. | Sapon. equiv. | Iodine value |
|---|---|---|---|---|---|---|---|---|---|---|
| F. | $F_{11}$ | 60-110° | 6·0g. | 226 | 56·8 | $F_2$ | 146° g. | 21·5 g. | 294·8 | 165·4 |
| | $F_{12}$ | 110-140 | 5 0 | 230 | 8·2 | $F_3$ | 146-150 | 15·5 | 294·3 | 168·2 |
| | $F_{13}$ | 145 | 4·5 | 287 | 134·5 | $F_4$ | 150-55 | 22 4 | 294·6 | 158·4 |
| | $F_{14}$ | 147-152 | 7 5 | 292 | 150·0 | $F_5$ | 155-175 | 13·5 | 294·7 | 138·7 |
| | FR | ... | 4·6 | 292 | 138·0 | FR | ... | 10·5 | 305·2 | 120·0 |

TABLE IV.

*Fractionation of ester* E.

| | B. p. | Wt | Sapon. equiv. | Iodine value. |
|---|---|---|---|---|
| $E_1$ | 78-150° | 6·8g. | 290·2 | 126·4 |
| $E_2$ | 145-147 | 8·9 | 292·6 | 140·2 |
| $E_3$ | 148 | 45·0 | 292·8 | 142·5 |
| $E_4$ | 148-152 | 35·0 | 296·4 | 140·4 |
| $E_5$ | 154 | 8·4 | 296·3 | 140·0 |
| ER | ... | 12·5 | 298 4 | 125· |

TABLE V.

*Fractionation of ester* S.

| | B. p. | Wt. | Sapon. equiv. | Iodine value. |
|---|---|---|---|---|
| $S_1$ | 98-130 | 2·8 g. | 258·2 | 23·2 |
| $S_2$ | 130-140 | 3·6 | 275·4 | 30·4 |
| $S_3$ | 145 | 2·4 | 280·0 | 35·6 |
| SR | ... | 3·4 | 304·1 | 20·5 |

FR. contained 3·4% of non-saponifiables.

Myristic acid (m.p. 52°); palmitic acid (m.p. 62°). and stearic acid (m.p. 68°) were identified from the various fractions of the solid acids by their mixed melting point with pure samples of these acids. The fractions of the liquid acids A and E were oxidised individually with alkaline permanganate (Lapworth and Moltram, *J. Chem. Soc.*, 1925, **127**, 1678), dihydroxystearic acid (m.p. 130°) and two tetrahydroxy acids, one melting at 154° and the other melting at 174°, were identified.

On extracting the oxidation products of fraction $F_1$. $F_2$ and $E_1$ solid saturated acids *e.g.* lauric acid (m.p. 42°), myristic acid (m.p. 52°) and a little palmitic acid (m.p 62°) were identified by their mixed melting point with pure samples. Fraction S*R* gave two acids on crystallisation from ethyl acetate, one melting at 71° which was identified to be archidic acid (mixed melting point with an authentic sample) and the other, melting at 75°, was identified to be lignoceric acid by mixed m.p. with pure lignoceric acid. No behenic acid could be isolated from any fraction of this oil.

10·2 G. of freshly prepared fatty acid were brominated in 100 c.c. of ether at about 0° after which it was left overnight in ice—chest. 0·031 G. of solid bromide, melting at 178°, was obtained which is calculated to be 0·108% linolenic acid in the oil.

The component fatty acids in the glycerides of safflower oil, obtained experimentally, are shown in Table VI.

TABLE VI.

| | Acid in A. 51·3% | Acid in E. 42·6 | Acid in S. 6·1 | % on mixed acids by wt. | % on mixed acids by mol.%. | | Acid in A. 51·3% | Acid in E. 42 6 | Acid in S. 6·1 | % on mixed acids by wt. | % on mixed acids by mol.%. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Lauric and lower acids | 0·39 | ... | ... | 0·4 | 0·6 | Archidic & lignoceric acid | ... | ... | 0·45 | 0·5 | 0·5 |
| Myristic acid | 0·20 | 0·06 | 0·85 | 1·1 | 1·3 | Oleic acid | 14·46 | 15·54 | 1·75 | 32·8 | 32·6 |
| Palmitic acid | 0·80 | 0·20 | 1·85 | 2 9 | 3 2 | Linolic acid | 35·35 | 25·80 | ... | 61 1 | 60·6 |
| Stearic acid | ... | ... | 1·1 | 1·1 | 1·1 | Linolenic acid | 0·1 | ... | ... | 0 1 | 0·1 |

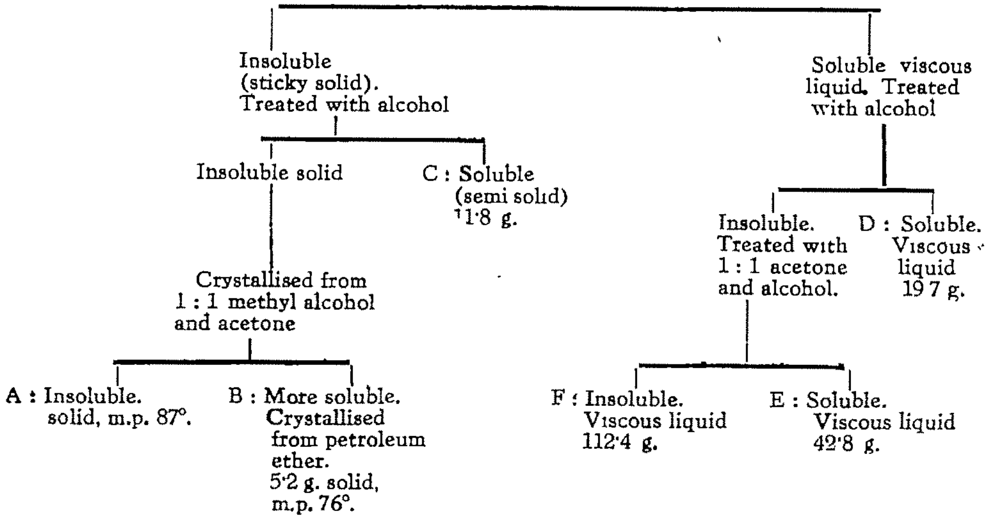
*Component Glycerides of Safflower Oil.*—Freshly expressed oil was rendered neutral by washing with sodium carbonate solution after which it was filtered through decolourising charcoal. This oil was used for the determination of the composition of the glycerides.

122·8 G. of oil were dissolved in 750 c.c. of acetone and left overnight at 0°. No precipitation occurred. This indicates the absence of fully saturated or disaturated glycerides. This oil was oxidised successively with powdered potassium permanganate after adding another 450 c.c. of acetone. Finally 0·62g. of a neutral product was obtained. On further examination it was found to be only non-saponifiable matter. Consequently this oil does not contain any fully saturated glyceride.

The neutral oil (100·2g.) was dissolved in one litre of petroleum ether and cooled down to −5°to+1°. Bromine was added to it slowly till the whole solution acquired a permanent brown colour. It was then left overnight in refrigerator. The precipitate was filtered and washed off with chilled petroleum ether. The filtrate was washed with sodium thiosulphate solution in order to get rid of bromine. After distilling off the solvent a viscous liquid was obtained which was further separated into different fractions by treating it with alcohol and 1 : 1 alcohol and acetone mixture. The solid was subsequently treated with alcohol and two fractions, one soluble in alcohol and the other insoluble in alcohol, were obtained. The alcohol-insoluble portion was again crystallised from 1 : 1 methyl alcohol and acetone. The portion more soluble in this solvent was crystallised from petroleum ether. A general scheme of separation is given in Table VII.

TABLE VII.

100·2 G· of oil in 1 litre petroleum ether brominated.



All these fractions were debrominated by boiling with zinc dust and hydrogen chloride in ethyl alcohol. The debrominated products were saponified and acids were liberated after extracting the non-saponifiables. The individual unsaturated acids were identified by oxidising them with alkaline potassium permanganate. The saturated acids were extracted with petroleum ether from the oxidation products of these fractions. As the saturated acids in each fraction were too small in quantity to enable the separation of the individual acids, all the saturated acids of a particular fraction were considered as one and the mean molecular weights or the saponification equivalents were determined. The proportions of the unsaturated acids were determined from the saponification equivalent, iodine values and thiocyanogen values.

Fraction A was too small in quantity for all the tests that were carried with the other fractions Consequently the bromine content of this fraction was determined according to the method of Bacons (*Chem News*, 1909, **99**, 6). (Found : Br, 56·14. Calc. $C_{57}H_{98}O_6Br_2$ : Br, ·49·63 per cent) The quantity of bromine estimated is more than that calculated for trilinolin and the melting point as well is higher than that observed in the previous case (*J. Indian Chem. Soc.*, 1940, **17**, 92) and in fraction B. It might be due to two reasons? First a small quantity of linolenic acid might have formed monolinolenin-dilinolin or a small quantity of the highly unsaturated sterols might have been brominated along with the glycerides to give bromides insoluble in petroleum ether. The quantity was so small that further tests were not possible. As the major portion of this fraction appears to be trilinolin, other considerations have been given up and the whole fraction has been considered to be trilinolin. The analytical results of all the fractions are given in Table VIII.

TABLE VIII.

| | A | B | C | D | E | F | Total |
|---|---|---|---|---|---|---|---|
| Weight in g. | 1·2 | 5·2 | 11·8 | 19·7 | 42·8 | 112·4 | 193·1 g. |
| Saponification equivalent of the acids | ... | 282·4 | 272 | 275·3 | 282 3 | 281·6 | |
| Iodine value | ... | 183·6 | 122·7 | 91·8 | 135·2 | 149·5 | |
| Thiocyanogen value | ... | 90·2 | 62·2 | 60·1 | 90·4 | 90 4 | |
| Weight of the debrominated glycerides | 0·51 | 2·5 | 6·65 | 12·4 | 23·2 | 57·5 | |
| Free from non-sap. (wt of non-sap.) | 0·04 | 0 38 | 0·004 | 0·008 | 0·45 | 0·12 | |
| % Glycerides free from non-sap. | 0·50 | 2 3 | 6·5 | 12·2 | 22·2 | 56·3 | |
| Saponification equivalent of the saturated acids. | ... | ... | 253 | 248 | Trace | ... | |

From these analytical results the molecular proportions of the various acids in each fraction were calculated. These are given in Table IX.

TABLE IX.

| | Mol % of the acids in each fraction. | | | | | | | Mol % of the acids in the fraction on total acids. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acids | A | B | C | D | E | F | Mean. | A | B | C | D | E | F | Mean. |
| Oleic acid | ... | . | 3 | 31 1 | 56·5 | 34·5 | 35·09 | ... | ... | 0·19 | 3·8 | 11·7 | 19·4 | 35·09 |
| Linolic acid | 100 | 100 | 66 | 35 6 | 43·5 | 65·5 | 58·65 | 0·5 | 2·3 | 4·15 | 4·3 | 10·5 | 36·9 | 58·65 |
| Saturated acids | ... | ... | 31 | 33·3 | Trace | ... | 6·26 | ... | ... | 2·16 | 4·1 | Trace | ... | 6·26 |

The composition of the fatty acids obtained by the bromination of the oil agrees with that obtained by ester fractionation method.

The component glycerides of the safflower oil have been calculated from these results and are given in Table X.

TABLE X.

| Fractions. | 0·5 A | 2·3 B | 6·5 C | 12·2 D | 22·2 E | 56·3 F | Total |
|---|---|---|---|---|---|---|---|
| 1. Fully saturated glyceride | Nil | Nil | Nil | Nil | Nil | Nil | Nil |
| 2. Disaturated glycerides | ... | ... | ... | ... | ... | ... | Nil |
| 3. Monosaturated glycerides : | | | | | | | |
| (*a*) monosaturated dilinolin | ... | ... | 5·8 | 0·8 | ... | ... | 6·6 |
| (*b*) monosaturated oleo-linolin | ... | | 0·6 | 11·4 | | | 12·0 |
| 4. Tri-unsaturated glycerides : | | | | | | | |
| (*a*) Dioleolinolin | ... | ... | ... | ... | 12·9 | 1·9 | 63·7 |
| (*b*) Oleodilinolin | ... | ... | ... | ... | 9·3 | 54·4 | 14·8 |
| (*c*) Trilinolin | 0·5 | 2·3 | 0·1 | ... | ... | ... | 2·9 |

The proportion of the various saturated acids in the oil is already known. On the assumption that all the saturated acids have distributed themselves as oleo-linoleo-saturated glycerides and dilinoleo-saturated glycerides in the same proportion as these glycerides exist in the oil, the component glycerides of the safflower oil may be regarded approximately as :—mono-myristo-oleolinolin 2%, monopalmito-oleolinolin 7%, monostearo-oleolinolin 2%, myristodi-linolin 1%, palmitodilinolin 4%, stearo-dilinolin 1%, dioleolinolin 15% and oleodilinolin 63%.

The myristo glyceride contains a little of lauric and other lower acids and stearo glycerides contain little of archidic and lignoceric acids.

The component fatty acids of the Indian safflower seed oil are compared here with those of the two varieties of American (Jamieson and Gertler, *Oil & Fat Ind.*, 1929, **6**, No. 4, II ; Vanloon, *Verf. Kronick*, 1937, **10**, 80) and one variety of Mid Asiatic oil (Zuckerwanik, *Acta Univ. Asiae. Medic*, 1938, **6** No. 2, 3, 14].

TABLE. XI.

| | American | | Mid Asiatic. | Indian. | | American. | | Mid Asiatic. | Indian. |
|---|---|---|---|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | | 1. | 2. | 3. | 4. |
| Saturated acids | 6·25 | 8·6 | 8·9 | 6 | Linolic | 67·4 | 71·3 | 39-50 | 61·1 |
| Oleic | 26·2 | 16·7 | 34·37 | 32·8 | Linolenic | 0·15 | 3·4 | 0·5 | 0·1 |

Both the samples of the American safflower oils, grown in temperate climate, are richer in the acids having two or three ethylenic linkages, compared to the Mid Asiatic and Indian oils, as expected according to Ivanov's hypothesis (*loc. cit.*). The 2nd sample of the American oil appears to contain exceptionally high percentage of linolic and linolenic acid which may either be due to the different variety of seed or to the difference in climate and soil of the area where it might have been grown.

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# PYRONES AND RELATED COMPOUNDS. PART II. A NEW REACTION PRODUCT OF ACETONE DICARBOXYLIC ACID AND ACETIC ANHYDRIDE

By R Kaushal, P. B. Bhisse and S. S. Deshapande

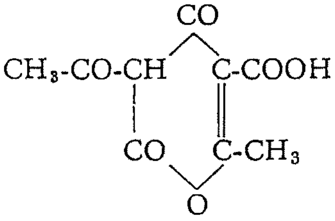
By the action of four molecules of acetic anhydride on one molecule of acetone dicarboxylic acid a new acid, $C_9H_6O_5$, is obtained, to which a tentative structure is assigned.

The action of acetic anhydride on acetone dicarboxylic acid is known to give the following products :

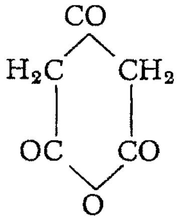
(*i*) Dehydracetocarboxylic acid (I) (Pechmann and Neger, *Annalen*, 1893, **273**, 186).

(*ii*) Acetone dicarboxylic anhydride (II) and the mixed anhydride (III) of acetone dicarboxylic acid and acetic acid (Willstätter, *Annalen*, 1922, **428**, 422).

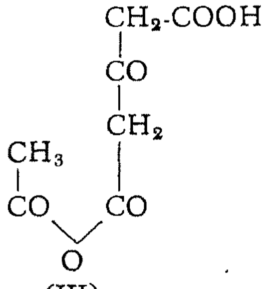
(*iii*) Dihydroxypyrone (IV), isolated by one of us (*J. Indian Chem. Soc.*, 1940, **17** 138).



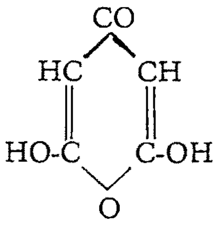
(I)



(II)



(III)



(IV)

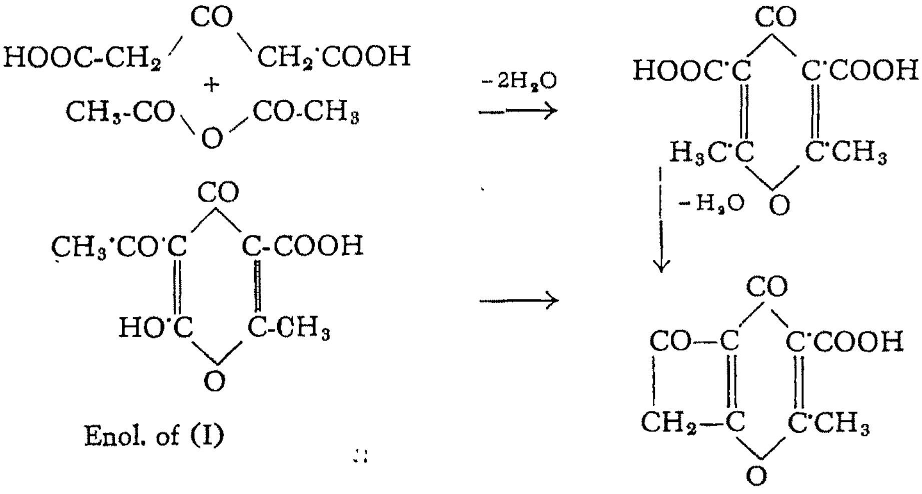
In one of the somewhat large scale preparation of dihydroxypyrone (IV) a new acid, m.p. 154°, has been obtained.

From the melting point it was thought to be identical with dehydracetocarboxylic acid (I, m.p. 154°), but a comparison between the two revealed some differences in their physical and chemical properties. Both are acids. The compound (I) dissolves in aqueous potash and on adding excess of acetic acid to the alkaline solution, the mono-potassium salt of the acid separates (Pechmann and Neger, *loc. cit.*). The new acid, however, behaves differently.

The new acid, $C_9H_6O_5$, seems to have been formed from one molecule of acetone dicarboxylic acid and one molecule of acetic anhydride by elimination of three molecules of water.

$$C_5H_6O_5 \quad + \quad C_4H_6O_3 \quad = \quad C_9H_6O_5 \quad + \quad 3H_2O$$

The structure of the acid seems to be (V) formed in the following manner (*cf.* Phillippi and Seka, *Ber.*, 1921, 54B, 1089).



Enol. of (I)

(V)

This is confirmed by the fact that dehydracetocarboxylic acid (I) on crystallisation from acetic anhydride gives a solid whose melting and the mixed melting point with the acid (V) was found to be 157°. But the reverse change from (V) to (I) could not be realised so far.

## EXPERIMENTAL

100 G. pure acetone dicarboxylic acid were treated with 200 g. of acetic anhydride. As usual the pyrone separated after standing overnight and was removed by filtration. The mother-liquor was allowed to evaporate at room temperature. From the resulting solid a second crop of the pyrone was obtained and another substance which after purification melted at 154°. It dissolves in aqueous potash and from the solution on standing its potassium derivative separates without addition of acetic acid. The potassium derivative was filtered at the pump, washed with a little dilute alcohol and dissolved in water. A part of the aqueous solution of the potassium derivative was acidified with hydrochloric acid when the new acid precipitated. It was filtered, washed with water and crystallised from dilute alcohol, from which it separated as prisms melting at 157°. [Found : C, 54·8 ; H, 3·2 ; Equiv. by titration, 192 ; as silver salt, 188. $C_9H_6O_5$ requires C, 55·6 ; H, 3·1 per cent. Equiv,. 194. $C_9H_8O_6$ (I) requires C, 50·9 ; H, 3·7 per cent].

Its aniline salt was prepared by dissolving equimolecular quantities of the acid and the aniline separately in ether and mixing the two solutions. The aniline salt precipitated at once. It was filtered, washed with ether and crystallised from alcohol as long yellow needles, m.p. 185°. (Found : C, 62·9 ; H, 4·4 ; N, 52. $C_{16}H_{13}O_5N$ requires C, 62·9 ; H, 4·8 ; N, 4·9 per cent).

When acetone dicarboxylic acid (one molecule) was treated with four molecules of acetic anhydride in the manner in which the dihydroxypyrone is prepared (*loc. cit.*), the sole product of the reaction is the acid (V), m.p. 157°.

In the formation of the dihydroxypyrone one molecule of water is eliminated from one molecule of acetonedicarboxylic acid, as such the preparation of the dihydroxy pyrone was modified since the publication of the paper (*loc. cit.*).

On addition of acetonedicarboxylic acid (one molecule) to two molecules of acetic anhydride instead of two and half molecules, the acid went into solution as usual with the evolution of heat. After allowing it to remain for 4 hours and seeding the dihydroxypyrone separated as small shining plates. This was left overnight and the next day it was filtered, washed and dried ; yield however improved a little. In this manner 20 g. of acetone dicarboxylic acid gave 12·5 g. of dihydroxypyrone.

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# MOLAR REFRACTION AND THE STRUCTURE OF OXYMETHYLENE KETONES

By R. Kaushal

The values of the molar refraction of ethoxymethylene acetone and ethoxymethylene methylethyl ketone are recorded and the results confirm the structure assigned to oxymethylene acetone and oxymethylene methylethyl ketone on other grounds.

On physicochemical evidence oxymethylene acetone and oxymethylene methylethyl ketone are shown to possess the structure (I) and (II) (R = H) (*cf.* Kaushal, Sovani and Deshapande, *J. Indian Chem. Soc.*, 1942, **19**, 108 ; Joshi, Kaushal and Deshapande, *ibid.*, 1941, **18**, 479)

$CH_3$-CO-CH : CH-OR (I)

$CH_3$-CO-C($CH_3$) : CH-OR (II)

The molecule of (I) or (II) possesses a conjugated double bond, and their molar refraction has been studied. Oxymethylene acetone is unstable and oxymethylene methylethyl ketone is a solid, m.p. 72° (*loc. cit.*) Hence to study the molar refractions their ethyl ethers have been prepared by condensing the crude sodio derivatives of (I) or (II) with ethyl halide in alcoholic suspension.

## EXPERIMENTAL

*Ethoxymethylene acetone* (I, R = $C_2H_5$) was prepared by treating the sodium oxymethylene acetone (from 12 g. acetone, 20 g. formic ester and 5 g. sodium wire in dry ether) with 37 g. of ethyl bromide in 250 c. c. of absolute alcohol and allowing it to remain for 48 hours. It was then refluxed on a water-bath for 8 hours with more ethyl bromide (10 g.). The sodium bromide separating was filtered off and the excess of alcohol distilled. The residue was shaken with water and made nearly neutral with dilute sulphuric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulphate and on distilling off the excess of chloroform 12 g. of crude product were obtained which on distillation under reduced pressure gave pure ethoxymethylene acetone as a very light pale yellow coloured liquid, b. p. 74-76°/6 mm. [Found : C, 63·2 ; H, 9·2 ; Equiv., 110 (back titration). $C_6H_{10}O_2$ requires C, 63·5 ; H, 8·8 per cent. Equiv., 114).

It gives red colour to ferric chloride which deepens on standing. It is not acidic to litmus but gradually shows acid reaction to moist litmus due to hydrolysis into oxymethylene acetone (*cf.* Claisen, *Annalen*, 1897, **297**, 1).

With aniline and zinc chloride it forms the *anilide* $CH_3$-CO-CH : CH·NH Ph. as a gummy product which after purification melts at 247°. (Found : N, 8·3. $C_{10}H_{11}ON$ requires N, 8·7 per cent).

By keeping in contact with semicarbazide hydrochloride, sodium acetate and alcohol for 48 hours it formed the *oxymethylene acetone* bis-*semicarbazone*, which crystallises from alcohol and melts at 242°. (Found : N, 41·5. $C_6H_{12}O_2N_6$ requires N, 42·0 per cent) (*cf.* Wallach, *Annalen*. 1903, **329**, 131).

*Ethoxymethylene methylethyl ketone* (II, $R = C_2H_5$) was prepared in a manner similar to ethoxymethylene acetone. Thus the sodium compound from 12·5 g. methylethyl ketone, 18·6 g. formic ester and 5·8 g. sodium wire, with ethylbromide (33 g. + 10 g.) gave 5g. pure ethoxymethylene methylethyl ketone, b. p. 79°/8 mm. If, however, after removal of alcohol, the residual liquid was worked without making the solution nearly neutral, the yield increased to 7 g. and the colour of the product did not change to reddish as in the former preparation. [Found : C, 65·2 ; H, 9·6 ; Equiv., 130 (back titration). $C_7H_{12}O_2$ requires C, 65·6 ; H, 9·4 per cent. Equiv., 128).

It is a thin colourless liquid with a pleasant odour, is not acidic to litmus but after sometime shows acid reaction to moist litmus due to hydrolysis of -OEt into OH. It gives a faint violet colour to ferric chloride which deepens on standing or on heating. On prolonged contact with semicarbazide, alcohol and water it gave a solid (m.p. 260°) in very poor yield.

### *Refractivity Measurements.*

The densities of the double distilled liquids were determined by a small pyknometer at 33° using the formula :—

$$d_4^t = \frac{W'D}{W} - \frac{0{\cdot}0012(W' - W)}{W}$$

where $d_4^t$, density of liquid at $t°$ referred to water at 4° ; $W'$, weight of liquid filling pyknometer ; $W$, weight of water filling pyknometer and $D$, density of water at $t°$ (at 33°, 0·9959).

The refractive indices were measured by Abbey's refractometer and molar refracrions calculated by Lorenz and Lorenz formula using Bruhl's values of atomic refractions. $M_D = \frac{n^2 - 1}{n^2 + 2} \times \frac{m}{d}$ where '*n*', is refractive index ; '*m*', molecular weight and '*d*', the density of the liquid.

For *ethoxymethylene acetone* $d_4^{33}$ = 0·93018 ; $n_D^{33}$ = 1·6075 and therefore $M_D$ = 41·9 ; formula (I, R = $C_2H_5$) requires $M_D$, 31·04.

For *ethoxymethylene methylethyl ketone* $d_4^{33}$ = 0·93876 ; $n_D^{33}$ = 1·4535 and therefore $M_D$ = 36·9 ; formula (II, R = $C_2H_5$) requires $M_D$, 35·6.

## DISCUSSION.

Ethoxymethylene acetone possesses a simple conjugated system and as such it gives a pronounced exaltation in the value of its molar refraction. But in the case of ethoxymethylene methylethyl ketone, the conjugation is not simple as in the case of its lower homologue. Had the structure of ethoxymethylene methylethyl ketone been (I, R = $C_2H_5$ and $CH_3$ replaced by $C_2H_5$) *i.e.* $C_2H_5CO\text{-}CH : CH\text{-}OC_2H_5$, it would have shown similar exaltations in the value of its molar refraction.

It is therefore due to the methyl group marked with asterisk that the exaltations are not noticed even through the molecule contains a conjugated system. This is the effect of the methyl group in producing what Auwers and Eisenlohr terms 'Storung' or diminution of exaltations (Cohen, "Organic Chemistry", Vol II. p. 35) and every disturbance of conjugation by substituents diminishes the exaltations.

Hence oxymethylene acetone and oxymethylene methylethyl ketone are correctly represented by the formula (I) and (II) (R = H).

The author wishes to express his gratitude to Prof. S. S. Deshapande for his kind interest and to the Holkar Government for the facilities for work.

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# THE EFFECT OF H-ION CONCENTRATION ON THE VISCOSITY CHANGES IN THORUM PHOSPHATE GEL-FORMING MIXTURES DURING SETTING

By Miss A. Nathan

The investigation deals with the measurement of changes in viscosity taking place during the setting of thorium phosphate gel-forming mixtures of different $p_H$. It has been found that the rate of change of viscosity with time increases when the $p_H$ is reduced up to a certain value; further reduction in $p_H$ causes a decrease Two sets of straight lines are obtained when values of log $(\eta-\eta_0)$ are plotted against $t$, one set corresponding to mixtures having $p_H$ values ranging from the maximum to that of the mixture setting in minimum time and the other to those having lower $p_H$. The effect of the addition of increasing amounts of ethyl alcohol to mixtures having $p_H$ greater and less than that of the mixture setting in minimum time has been found to be different and it is surmised that this behaviour indicates the difference in the structures.

Several workers have studied the changes in viscosity occuring in a gel-forming system during gelation. Most of the work of this nature on inorganic gel-forming system has been carried out by Prasad and co-workers (*J. Phys. Chem.*, 1932, **36**, 1384). In these studies very little systematic work has been done on the viscosity changes with time during the setting of gels having different H-ion concentrations. In the present investigation an attempt has been made to measure the viscosity changes during the setting of thorium phosphate gels from mixtures of different H-ion concentrations. Mehta, Parmar and Prasad (*J. Indian Chem. Soc.*, 1936, **13**, 128) have studied the effects of the addition of increasing amounts of hydrochloric, nitric and sulphuric acids on the viscosity changes during the setting of thorium phosphate gels and have found that such an addition of the first two acids increases the rate of change in viscosity with time, while with the third one, the rate at first decreases and then increases.

## EXPERIMENTAL

Scarpa's method employed by Prasad and Modak (*Proc. Indian Acad. Sci.*, 1940, **A 11**, 282) was used in this investigation. The diameter and the length of the capillary tube were 0·0995 cm. and 4·395 cm. respectively, and the volume of the bulb between the two marks was 1·72 c.c. The pressure applied for suction was 20 cm. of water and was kept constant throughout. The constant of the apparatus was determined by using sucrose solution and was found to be 0·00218.

The concentrations of solutions of thorium nitrate, phosphoric acid and hydrochloric acid used were 6% (*N*/2), 2*N* and 2*N*, respectively. They were prepared in the same manner as described by Nathan (to be published in a later issue of this Journal).

The chosen constituents of the gel-forming mixture were taken in two separate test-tubes which were placed in the thermostat maintained at 35°±0·02, till they acquired the temperature of the bath. They were then mixed in the manner described by Nathan (*loc. cit.*) and the mixture was poured in the viscosity bottle.

## TABLE I.

$y = 0·0$ c.c.
$p_H = 1·42$

| t. | η. |
|---|---|
| 61·5 sec. | 3·781 |
| 125 | 4·105 |
| 197 | 4·609 |
| 581 | 4·766 |
| 664 | 4·784 |
| 726 | 5·055 |
| 788 | 5·333 |
| 1267 | 6·610 |
| 1596 | 7·335 |
| 1853 | 7·885 |
| 2077 | 8·109 |
| 2150 | 8·421 |
| 2478 | 9·210 |

$y = 0·20$ c.c.
$p_H = 1·00$

| t. | η. |
|---|---|
| 65 sec. | 4·664 |
| 123 | 5·219 |
| 250 | 5·824 |
| 388 | 5·864 |
| 425 | 6·493 |
| 532 | 7·701 |
| 615 | 8·420 |
| 732 | 9·390 |
| 833 | 10·330 |
| 985 | 12·110 |
| 1087 | 13·450 |
| 1212 | 15·220 |
| 1340 | 17·570 |
| 1517 | 20·390 |
| 1722 | 24·250 |
| 1987 | 30·200 |
| 2525 | 43·020 |

$y = 0·50$ c.c.
$p_H = 0·79$

| t. | η. |
|---|---|
| 204 sec. | 6·666 |
| 272 | 8·110 |
| 362 | 9·544 |
| 462 | 11·950 |
| 626 | 15·930 |
| 783 | 20·900 |
| 949 | 28·610 |
| 1252 | 41·270 |
| 1617 | 63·980 |
| 2273 | 101·900 |
| 3142 | 210·300 |

$y = 0·75$ c.c.
$p_H = 0·68$

| t. | η. |
|---|---|
| 75 sec. | 5·883 |
| 116 | 7·220 |
| 290 | 11·110 |
| 405 | 14·510 |
| 531 | 19·760 |
| 707 | 28·020 |
| 594 | 42·800 |
| 1402 | 71·650 |

$y = 1·00$ c.c.
$p_H = 0·50$

| t. | η. |
|---|---|
| 67 sec. | 6·107 |
| 143 | 77·817 |
| 229 | 12·220 |
| 339 | 16·220 |
| 485 | 23·440 |
| 735 | 40·370 |
| 1820 | 108·300 |
| 3215 | 204·500 |

$y = 1·50$ c.c.
$p_H = 0·45$

| t. | η. |
|---|---|
| 69 sec. | 8·211 |
| 159 | 13·020 |
| 313 | 26·510 |
| 645 | 56·400 |

$y = 2·00$ c.c.
$p_H = 0·30$

| t. | η. |
|---|---|
| 76 sec. | 10·500 |
| 165 | 16·380 |
| 317 | 27·850 |
| 770 | 73·480 |
| 1230 | 130·000 |

$y = 2·50$ c.c.
$p_H = 0·26$

| t. | η. |
|---|---|
| 96 sec. | 17·120 |
| 320 | 40·330 |

$y = 3·00$ c.c.
$p_H = 0·200$

| t. | η. |
|---|---|
| 154 sec. | 33·430 |
| 737 | 88·110 |
| 1350 | 157·000 |

$y = 3·50$ c.c.
$p_H = 0·09$

| t. | η. |
|---|---|
| 159 sec. | 47·810 |
| 515 | 65·720 |
| 1212 | 110·300 |

$y = 4·00$ c.c.
$p_H$ = low

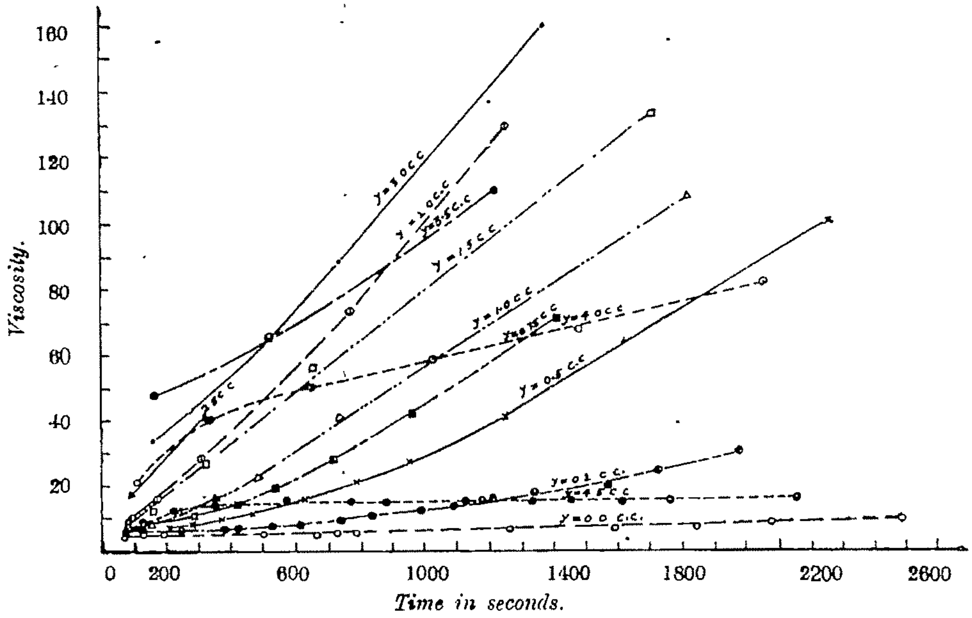
| t. | η. |
|---|---|
| 119 sec. | 20·900 |
| 335 | 40·380 |
| 647 | 50·500 |
| 1019 | 58·000 |
| 1472 | 68·560 |
| 2045 | 83·000 |
| 2857 | 100·900 |

$y = 4·54$ c.c.
$p_H$ = very low.

| t. | η. |
|---|---|
| 54 sec. | 5·332 |
| 119 | 8·120 |
| 204 | 12·010 |
| 342 | 13·450 |
| 557 | 14·200 |
| 765 | 14·200 |
| 877 | 14·540 |
| 1018 | 14·630 |
| 1175 | 14·900 |
| 1332 | 15·050 |
| 1451 | 15·050 |
| 1662 | 15·200 |
| 1767 | 15·200 |
| 2152 | 15·500 |

Viscosity readings (expressed in millipoises) were taken after known intervals (*t*, expressed in minutes) from the time of mixing and the results obtained are given in Table I in which *y* represents c.c. of 2*N*-HCl added to the mixture. These results and are shown in Fig. 1. The measurement of the viscosity in each case was continued until the mixture would not flow through the capillary tube of the viscometer.

FIG. 1.



# DISCUSSION

Various viscosity-time curves in Fig. 1, though similar in shape, have different slopes. This shows that some gels have a tendency to set quicker than others.

It was observed that after a certain time some gel-forming mixtures had become so viscous that the measurement of viscosity was rendered impossible. This was particularly observed with mixtures containing 0·3 c.c. of phosphoric acid, and hence in this case, the viscosity changes for only a limited number of mixtures have been measured.

It will be observed that with an increase in the amount of HCl in the gel-forming mixture containing 0·2 c.c. of phosphoric acid, the rate of change of viscosity increases with an addition up to 3·0 c.c. of HCl, that is, with a decrease in $p_H$ from 1·42 to 0·20. Further reduction in $p_H$, caused by further addition of HCl, causes a decrease in the rate of change of viscosity with time. The same has been found to be the case with gels prepared in presence of 0·3 c.c. of phosphoric acid, the change from the increase in the rate of change of viscosity with the progress of gelation to a decrease seems to take place with the mixture having $p_H$ 0·75.

If we take as a basis of comparison the time taken by the gel to attain a certain viscosity and take this time as proportional to the time of setting of the gel, we can follow the setting of these gels in the same manner as determined by the actual measurement of the time of setting. The time required to attain a viscosity of 70 millipoises was read from Fig. 1 in the case of all mixtures and these values have been plotted against the c.c. of HCl present in the mixtures. The curve obtained is shown in curve I, Fig. 2 and the corresponding data are given in Table II.

FIG. 2.

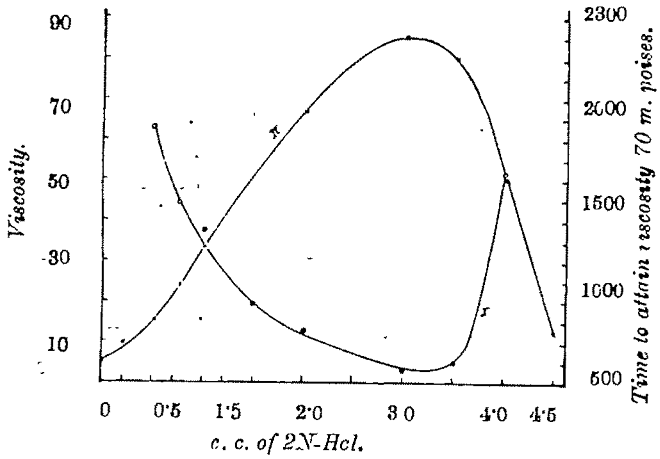


FIG. 3.

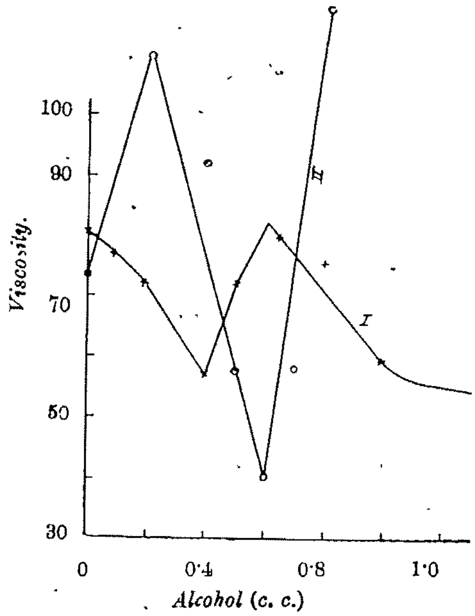


TABLE II.

| HCl. | Time. | HCl. | Time. |
|---|---|---|---|
| 0·50 c.c. | 1750 sec. | 2·00 c.c. | 750 sec. |
| 0 75 | 1390 | 3·00 | 560 |
| 1·00 | 1250 | 3 50 | 600 |
| 1·50 | 890 | 4·00 | 1520 |

TABLE III.

| HCl. | Viscosity. | HCl. | Viscosity. | HCl. | Viscosity |
|---|---|---|---|---|---|
| 0·00 c.c. | 5·0 | 1 00 c.c. | 38·0 | 3·00 c.c. | 86·0 |
| 0·20 | 8·0 | 1·50 | 56 0 | 3·50 | 80·0 |
| 0 50 | 18·0 | 2·00 | 64·0 | 4·00 | 52 0 |
| 0·75 | 28·0 | 2·50 | ... | 4·50 | 15 0 |

It will be noted that the values for mixtures containing no HCl and for those containing 0·2 c.c. and 4·5 c.c. of the acid, have not been given in the above table, because in these cases the maximum value of viscosity, when the flow in the capillary tube could not be observed, took place after a long time and the shape of the curve was consequently very flat. It will be seen from the nature of the curve in Fig. 2, that it is not different from the curve obtained by plotting the time of setting of the mixture containing 5·0 c.c. of the thorium nitrate and 0·3 c.c. of phosphoric acid, against c.c. of 2*N*-HCl added to the mixture (*cf.* Nathan, *loc cit.*). There is the similar flat minimum which would be expected. These results are very interesting in showing that even before the formation of firm gel takes place, the nature of the changes brought about by the addition of HCl is similar.

Alternatively the same information regarding the effect of the addition of HCl to the same gel-forming mixture, as given above, could be obtained by noting the viscosities of the several gel-forming mixtures at a given interval of time after mixing. The applicability of these views in the present case has been shown by reading the values of viscosity from the various curves in Fig. 1, at an interval of 700 seconds from the time of mixing. The values thus obtained are given in Table III and shown graphically by curve II in Fig. 2. This time interval is selected because in most cases the viscosity-time curve is straight, and hence represents a certain amount of regularity of viscosity changes with time.

It will be observed from curve II, Fig 2 that the viscosity at first rises, reaches a maximum value and then falls. Also the maximum viscosity value corresponds roughly with the minimum time of attaining a definite viscosity. This conforms to the view that even when a gel does not set, the physicochemical changes taking place in it are of the same nature and it only requires a different method of examination to bring them out. This point is brought out even in a more striking manner in the following.

Nathan (*loc. cit.*) observed that the times of setting and even the minimum time of setting, for mixtures prepared from 0·2 c.c. of phosphoric acid and different amounts of HCl are too long. The volume of HCl which causes the mixture containing 0·20 c.c. of phosphoric acid to set in minimum time can be calculated from the relation, $y=4-6x$, which has been found to hold with several mixtures. This value comes out to be 2·80 c.c. It will be seen from curves I and II in Fig. 2 that the volume of HCl corresponding to the minimum and maximum points in the curves is 3·0 c c. The observed result is therefore in very good agreement with the calculated one. In other words this method can be employed to determine the conditions necessary for the setting of the gel in minimum time.

In order to determine the manner by which the viscosity of the gel-forming mixture changes with time, the value of the viscosity at zero time was obtained by extrapolating viscosity-time curves in Fig. 1, to zero time and the values of viscosity at definite intervals of time were read from the curves. The values of log $(\eta-\eta_0)$ at different intervals of time ($t$) for different mixtures containing 0·2 c.c. of phosphoric acid were plotted against $t$ and the curves obtained were found to be straight lines. This shows that the relation, $\eta-\eta_0=ae^{kt}$ is obeyed. Theser esults are in agreement with those obtained by previous authors (Mehta, Parmar and Prasad, *loc. cit.*). It is further noticed that the straight lines for all mixtures containing up to 3·0 c.c. of HCl form one bunch, while those with mixtures containing larger amounts of HCl form another. It will be remembered that 3·0 c.c. of HCl corresponds to the minimum time of setting. Hence it appears that two sets of lines are obtained when log $(\eta-\eta_0)$ is plotted against $t$, one for the mixtures corresponding to the volumes of HCl smaller than that corresponding to the minimum time and the other for the greater amounts.

Prasad, Mehta and Desai (*J. Phys. Chem.*, 1932, **36**, 1384) have found that alcohol have an accelerating effect on the rate of increase of viscosity of silicic acid gel-forming mixtures in alkaline and moderately acidic media (only within a very small range of the alcohol added) and a retarding one in fairly acidic medium.

Mehta, Parmar and Prasad (*loc. cit.*) found that the addition of non-electrolytes to thorium phosphate gel-forming mixtures decreases the rate of change of viscosity. Prasad and Shejwalkar (*J. Indian Chem. Soc.*, 1940, **17**, 508) and Prasad and Modak (*loc. cit.*) also found that the rate of change of viscosity with time of gel-forming mixtures studied by them, decreases with the addition of increasing amounts of alcohol.

In this study the effect of ethyl alcohol was examined on mixtures containing 0·20 c.c. of phosphoric acid and 0·5 and 4·0 c.c. of HCl. These two mixtures correspond to points before and after the minimum time of setting. Increasing amounts of ethyl alcohol were added to the mixtures in the same manner as described by Nathan (*loc. cit.*) and the results obtained were plotted graphically.

It is observed from the nature of these curves that the effect of the addition of increasing amounts of ethyl alcohol to the mixture containing 0·5 c.c. of HCl is different from that of the mixture containing 4·0 c.c. All the viscosity-time curves in the former case rise fairly steeply with their concavity towards the viscosity axis, while in the latter case the curves are fairly flat rising with their concavity towards the time axis. Further, with the addition of increasing amounts of alcohol the viscosity of the mixture containing 0·5 c.c. of HCl at first decreases, reaches a minimum value ; then it increases and reaches a maximum value and finally falls when the amount of alcohol in the mixture exceeds 0·70 c.c. On the other hand with similar addition of alcohol to mixture containing 4·0 c.c. of HCl, the viscosity at first increases, reaches a maximum value ; it then falls and reaches a minimum value and then increases again. Only a limited amount of alcohol could be added to this mixture. The viscosity curves, when the amount of alcohol is increased beyond 0·40 c.c., have a tendency to slope downwards, probably due to the separation of the particles in the gel-forming mixture.

The above mentioned results have been brought out in Fig. 3 in which the curves I and II have been obtained on plotting the viscosity attained at 1800 seconds after mixing the gel-forming constituents against the c.c of alcohol added to the two mixtures, containing 0·5 and 4·0 c.c. of HCl, respectively. The difference in the structure of the gels forming from mixtures having the time of setting lower and higher than the minimum time of setting is thus brought out from the effect of the addition of alcohol on the viscosity changes with time of these mixtures. It may be noted that these results are essentially different from those obtained by previous workers (Mehta, Parmar and Prasad, *loc. cit.*).

The author feels grateful to Dr. Mata Prasad for suggesting the problem and the guidance throughout the progress of the work.

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# A STATISTICAL STUDY OF THE VARIATION OF SPECIFIC CONDUCTIVITY WITH CONCENTRATION OF ELECTROLYTES IN AQUEOUS SOLUTION

By Rama Gopal

When specific conductivity $\mu$ of aqueous solutions of electrolytes is plotted against the percentage concentration $c$, in a large number of cases it has been observed that the curve passes through a maximum which lies in most cases between 20% and 30% concentration. On a statistical study it has been found that electrolytes, in general, can be grouped into two broad divisions. The first one includes electrolytes without a maximum in the conductivity-concentration ($\mu$-$c$) curves: to this category belong the alkali (except Li) and ammonium salts of inorganic acids (HCl, $HNO_3$, $H_2SO_4$, HBr and HI). To the second class belong most of the soluble electrolytes e.g. LiCl, $CuCl_2$, $Cu(NO_3)_2$, $CuSO_4$, $CaCl_2$, $Ca(NO_3)_2$, and $ZnCl_2$ etc, all the acetates, carbonates, acids, and hydroxides etc. It has been further observed that, in general, for the same anion and different cations the maximum occurs at almost the same equivalent percentage concentration. An attempt has been made to explain the above facts on the ionic hydration hypothesis as modified in the light of recent theories.

In connection with some work on supersaturation, the specific conductivities of aqueous solutions of $KNO_3$, KCl, $K_2SO_4$ and sodium acetate were determined at different temperatures on the lines followed by Heim (*Ann. physikal. Chem.*, 1886, *iii*, 27, 613). While the specific conductivity—concentration curves at a given temperature were found to be straight lines in the first three cases, the curves for sodium acetate given below in Fig. 1 passed through a maximum at all the five temperatures tried. The maximum observed appeared to have nothing to do with the saturation or labile temperatures and it was always found to lie somewhere near 24% concentration which increased slightly with temperature.

TABLE I.

| Sulphates. | | | Chlorides. | | | Nitrates | | |
|---|---|---|---|---|---|---|---|---|
| | % Composition | | | % Composition. | | | % Composition. | |
| | Max. | Min. | | Max. | Min. | | Max. | Min. |
| *Cu | 22·5% | 0·2900 | Li | 18·0% | 0·4216 | *Mg. | 22·5% | 0·3102 |
| Zn | 24·0 | 0·2970 | Mg | 20·0 | 0·4246 | Ca | 25·0 | 0·3048 |
| Cd. | 30·0 | 0·2885 | Ca | 23·0 | 0·4144 | Sr | 30·0 | 0·2840 |
| Mg | 17·5 | 0·2910 | Mn | 23·0 | 0·3600 | Cu | 30·0 | 0·3199 |
| | | | Cu | 24·0 | 0·3600 | Cd | 35·0 | 0·2900 |
| | | | Cd | 25·0 | 0·2750 (?) | | | |
| | | | Zn | 27·0 | 0·4040 | | | |

* By extrapolation.

* By extrapolation.

It appears from the above table that the maximum in most cases lies between 20% and 30% concentration.

TABLE II.

| Inorganic acids. | | | Aliphatic organic acids. | | | Chloreacetic acids. | | |
|---|---|---|---|---|---|---|---|---|
| | % Composition. | | | % Composition. | | | % Composition. | |
| | Max. | Min. | | Max. | Min. | | Max. | Min. |
| Nitric | 30·0% | 0·4800 | Formic | 30·0% | 0·6510 | Acetic | 15·0% | 0·2490 |
| Hydrochloric | 19·0 | 0·5230 | Acetic | 15·0 | 0·2490 | Monchlor „ | 19·6 | 0·1961 |
| Sulphuric | 30·0 | 0·6120 | Propionic | 12·0 | 0·1700 | Dichlor „ | 22·5 | 0·1732 |
| Phosphoric | 46·0 | 1·5300 | Butyric | 11·0 | 0·2100 | Trichlor „ | 33·0 | 0·1700 |
| | | | Alkalis | | | | | |
| | % Composition. | | | % Composition. | | | % Composition. | |
| | Max. | Min. | | Max. | Min. | | Max. | Min. |
| KOH | 28·0% | 0·4988 | NaOH | 16·0% | 0·4000 | $NH_4OH$ | 5·0% | 0·3000 |

On referring to the literature a number of others electrolytes were found which exhibited this behaviour, while certain other appeared to be similar to KCl, $KNO_3$ and $K_2SO_4$. To the former type belong all the soluble acetates, carbonates, hydroxides and acids, soluble chlorides, sulphates, and nitrates of Li, Cu, Ca, Sr, Zn Al etc., while to the latter belong the sulphates, nitrates, chlorides, bromides and iodides of alkali (except Li) and ammonium cations.

In order to get further information about this behaviour, conductivity-concentration ($\mu$-$c$) curves, similar to those in Fig. 1, are obtained from data collected from Landolt-Bornstein Tables (Ed. 1912) and are given below.

FIG. 2.

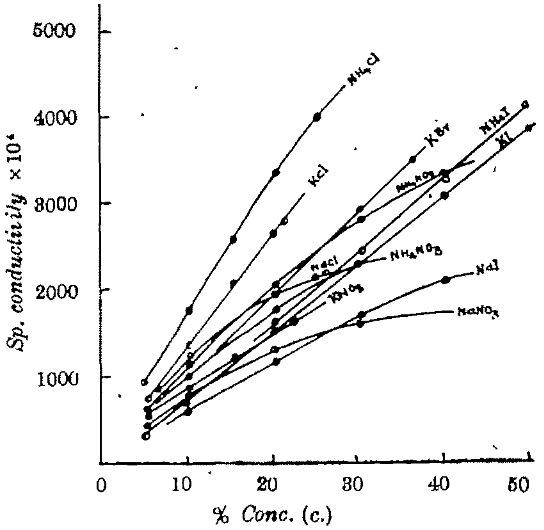
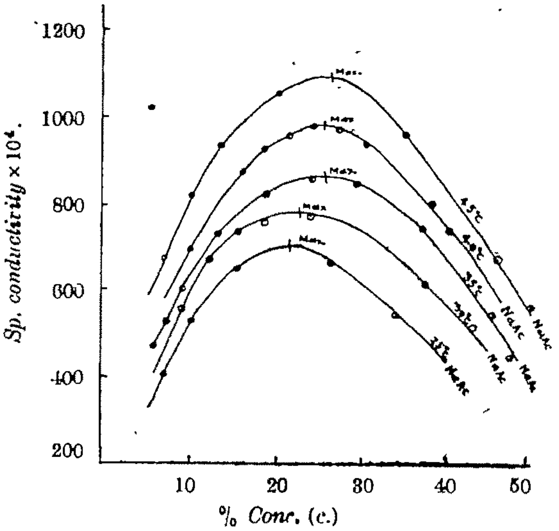


FIG. 1.



Similar curves have been obtained for a number of other electrolytes but only the results deduced therefrom are tabulated below along with those obtained for substances given in Figs. 2 and 3.

In all the tables given above, %. concentrations at the maximum, and at the maximum are in g. equivalents.

The curves and tables given above lead to the following conclusions :

Specific conductivity $\mu$ appears to shoot out in a straight line from the zero concentration. The later course of the curve depends, however, on the nature of the electrolyte in solution.

The $\mu$-$c$ curves, in general, pass through a maximum in all cases excepting the alkali and ammonium salts of inorganic acid. The curves for sodium and ammonium salts, however, have a tendency to bend towards the concentration axis (Fig. 2).

Sulphates, nitrates and chlorides of Cu, Li, Zn, Cd, and Mg etc. show that for the same anion and different cations the maximum, in general, occurs at approximately the same equivalent percentage concentration. For sulphates this concentration is 0·2900, for nitrates 0·3010, and for chlorides 0·4100 approximately.

The equivalent percentage concentration at the maximum for inorganic acids increases in the following order : $HNO_3 < HCl < H_2SO_4 < H_3PO_4$.

The maximum in the aliphatic organic acids occurs in the following increasing order : $C_3H_7COOH < C_2H_5COOH < CH_3COOH < H{\cdot}COOH$.

But this quantity for chloro-substituted acetic acids decreases with increasing amount of chlorine in the methyl group : $CH_3COOH > CH_2ClCOOH > CHCl_2.COOH > CCl_3COOH$ ; and for hydroxides it increases in the order : $NH_4OH < NaOH < KOH$·

## DISCUSSION

Crompton and Armstrong (*J. Chem. Soc.*, 1888, **53**, 116) were the first to recognise the maximum in the $\mu$—$c$ curves of aqueous solutions of a number of substances and took it to be an evidence of the existence of definite hydrates in solutions, thereby supporting the hydration hypothesis of Mendeleef (*Ber.*, 1886, **19**, 379 *et seq.*). But as the hydration theory of solutions was gradually replaced by the "Dissociation hypothesis" (*cf.* Arrhenius, *Phil. Mag.*, 1889, **28**, 3038), Crompton's suggestions could not be taken seriously. Later, Jones noticed the maximum in the $\mu$-$c$ curves of aqueous solutions of $CoCl_2$ and $CuCl_2$ in presence of different dehydrating agents and ascribed it to be due to increase in viscosity of solutions as a result of addition of dehydrating agents (Jones, "Hydrates in Aqueous Solutions", 1904, p. 840). However, this explanation is insufficient to cover all the facts pointed out herein, specially as it has been applied to solutions of mixtures of electrolytes of a particular nature but not to those of single substances.

Comparatively recently the researches of various authors have established the existence of hydrated ions in aqueous solutions. An attempt has been made below to show that the results arrived at from a close study of $\mu$—$c$ curves can be explained, in general, from the viewpoint of hydration of ions.

### *Ionic Interaction and the Hydrated Ions.*

As mentioned above the chlorides, nitrates, and sulphates of Na, $NH_4$ and K do not exhibit any maximum in the $\mu$—$c$ curves but the corresponding acids do. Also all the soluble acetates, carbonates and all the soluble salts of Ca, Cu, Cd, Zn, Fe, Al etc., in general, show the maximum. If the ionic interaction is the main cause of the fall in $\mu$ with increase in concentration then the maximum should also occur in the $\mu$-$c$ curves of alkali and ammonium salts of inorganic acids at approximately similar concentrations. Even allowing for the sizes of the ions, there must be some curvature in the curves of K-salts of inorganic acids as a result of electrical attraction. The almost straight line nature of these curves rules out the possibility of any major effect of interionic attraction which, however, can not be totally neglected and it will certainly play a susidiary rôle in reducing $\mu$ with increase in $c$. It may add to the hydration effect as both the phenomena appear to go hand-in-hand.

Various researches appear to show that, in general, $K^+$, $Na^+$, $NH^+_4$, $NO^-_3$, $SO_4^{--}$, $Cl^-$, $Br^-$, and $I^-$ ions have a smaller affinity for water molecules than $Li^+$, $Ca^{++}$, $Sr^{++}$, $Cu^{++}$, $Mg^{++}$, $Zn^{++}$, $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$ etc. Sudgen (*J. Chem. Soc.*, 1926, 174, 196) even goes to the extent of assuming that anions are not hydrated at all. The majority of workers consider, however, that at least $SO_4^-$ and F are hydrated. Apart from hydration hypothesis of Fajans and others, a more recent conception of hydration is obtained from the entropies of different ions in aqueous solutions. The following table (Rice, "Electronic Structure and Chemical Binding", 1940, p. 480) gives the entropies of different ions, which are supposed to be dissolved in water from gaseous state, in aqueous solution.

TABLE III.

| Ion. | $\Delta S$. | Ion. | $\Delta S$. | Ion. | $\Delta S$. | Ion. | $\Delta S$. |
|---|---|---|---|---|---|---|---|
| $H^+$ | $-24{\cdot}3$ | $Mg^{++}$ | $-70{\cdot}0$ | $Pb^{++}$ | $-40{\cdot}8$ | $I^-$ | $-4{\cdot}2$ |
| $Li^+$ | $-25{\cdot}3$ | $Ca^{++}$ | $-51{\cdot}2$ | $Fe^{++}$ | $(-69{\cdot}0)$ | $S^-$ | $-26{\cdot}2$ |
| $Na^+$ | $-19{\cdot}6$ | $Ba^{++}$ | $-41{\cdot}2$ | $Fe^{+++}$ | $(-112)$ | | |
| $K^+$ | $-11{\cdot}0$ | $Cu^{++}$ | $(-69{\cdot}0)$ | $Al^{+++}$ | $(-119{\cdot}2)$ | | |
| $Rb^+$ | $-8{\cdot}8$ | $Cd^{++}$ | $-59{\cdot}3$ | $F^-$ | $-26{\cdot}1$ | | |
| $Ag^+$ | $-20{\cdot}7$ | $Hg^{++}$ | $-51{\cdot}1$ | $Cl^-$ | $-12{\cdot}2$ | | |
| $Tl^+$ | $-9{\cdot}6$ | $Sn^{++}$ | $-48{\cdot}0$ | $Br^-$ | $-8{\cdot}6$ | | |

[ Figures in paranthesis are doubtful. ]

The above table reveals that $Na^+$, $K^+$, $Rb^+$, $Tl^+$, $Cl^-$, $Br^-$ and $I^-$ have higher entropy values ($+\Delta S$) as compared to $Mg^{++}$, $Cu^{++}$, $Sr^{++}$, $Ba^{++}$, $Ca^{++}$, $Cd^{++}$, $Fe^{++}$, $Al^{+++}$ etc., whereas $Li^+$ and $H^+$ have a value approximately half that of the most of the divalent cations Higher entropy means a greater freedom of movement in the medium *i.e.*, less attachment with the solvent molecules and hence less hydration and *vice versa*.

As entropy is an additive function, their values for the counter-ions of any salt can be added which should give, in general, the resultant hydration effect for that particular salt. By comparing these values for different salts, an idea of the relative hydration can be obtained as is clear from Table IV.

TABLE IV.

*Total ionic entropies of some halides.*

| Cation. | F. | Cl. | Br. | I. | |
|---|---|---|---|---|---|
| $Na^+$ | −45·7 | −31·8 | −28·2 | −23·8 | |
| $K^+$ | −37·0 | −23·2 | −19·6 | −15·2 | |
| $Rb^+$ | −34 9 | −21 0 | −17·4 | −13·0 | |
| $Tl^+$ | −35·6 | −21·8 | −18·2 | −13·8 | Group I |
| $H^+$ | −50·4 | −36·5 | −32 9 | −28·2 | |
| $Li^+$ | −51·4 | −37·5 | −33·9 | −29·5 | |
| $\frac{1}{2}Ca^{++}$ | −51·7 | −37·8 | −34·2 | −29·8 | |
| $\frac{1}{2}Mg^{++}$ | −61·1 | −47·2 | 43·6 | −39·2 | |
| $\frac{1}{2}Cu^{++}$ | −60·6 | −46·7 | −43·1 | −38·7 | Group II |
| $\frac{1}{2}Cd^{++}$ | −55·7 | −41·8 | −38·2 | −33·8 | Group I |
| $\frac{1}{3}Al^{+++}$ | −65·8 | −57·9 | −48·3 | −43·2 | |
| $\frac{1}{3}Fe^{+++}$ | −63·4 | −49·5 | −45·9 | −41 5 | |

TABLE V.

*Heats of hydration of halides of different cations.*

| Cation. | F. | Cl. | Br. | I. | |
|---|---|---|---|---|---|
| $Na^+$ | 242 8 | 203·6 | 192·1 | 181·2 | |
| $K^+$ | 223·6 | 184·3 | 172·9 | 162 2 | Group I |
| $Tl^+$ | 246·1 | 206·9 | 195·6 | 184 8 | |
| $Ag^+$ | 240·9 | 208·6 | 197·9 | 186·5 | |
| $Li^+$ | 276·3 | 237·1 | 225 9 | 215·2 | |
| $Mg^{++}$ | 750·0 | 672·3 | 649·7 | 630 0 | |
| $Ca^{++}$ | 650·9 | 570·2 | 547·9 | 526·1 | |
| $Sr^{++}$ | 620·3 | 540·1 | 517·8 | 496·4 | Group II |
| $Ba^{++}$ | 573 1 | 493·5 | 471·0 | 449·6 | |
| $Zn^{++}$ | ... | 731·2 | 708 6 | 688·9 | |
| $Cd^{++}$ | ... | 678·2 | 656·8 | 639 8 | |
| $Hg^{++}$ | ... | 698 1 | 677·0 | 666 0 | |
| $Pb^{++}$ | ... | 598·0 | 575 6 | 558·0 | |

It can be easily concluded from Table IV that alkali halides, in general, are less hydrated than other halides ($\Delta S <$ or $= -34$ approx.). Similar results are expected for the salts of other inorganic acids and above cations.

Assuming that a higher heat of hydration implies a greater affinity between water molecules and ions *i.e*, assuming that the Thomsen-Berthelot principle is applicable to such systems, a rough idea of the relative extent of hydration can be obtained from the works of Butler (*Z. physikal. Chem.*, 1924, **113**, 285) as is clear from Table. V.

To illustrate the above point consider the different halides of lithium. Li-ion is common in all cases (and hence its heat of hydration); obviously, then, the hydration of the halide ions occurs in the order: $F^- > Cl^- > Br^- > I^-$. Similarly by taking an anion common it may be seen that: $(Li^- > Tl^+ > Na^+ > Ag^+ > K^+) < (Zn^+ > Cd^+ > Mg^{++} > Hg^{++} > Pb^{++} > Ca^{++} > Sr^{++} > Ba^{++})$. It may be pointed out, however, that the values of the heats of hydration of ions have been obtained indirectly from the lattice energy and the heat of solution by the method developed by Fajans (*Ber. physikal. Ges.*, 1919, **21**, 549).

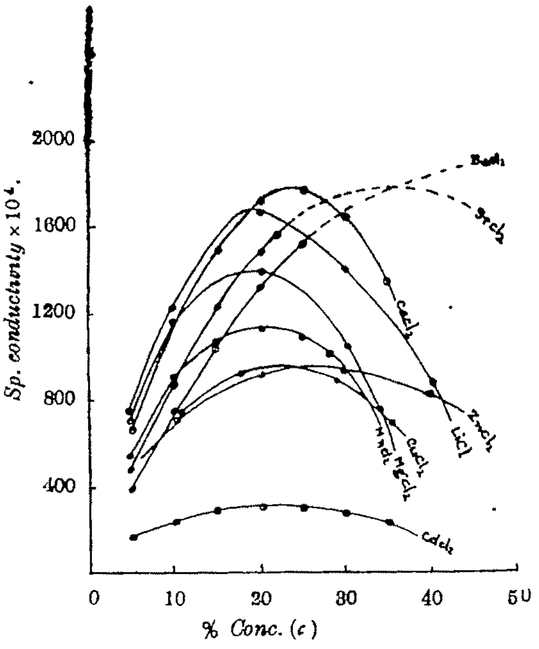
Assuming then, that the maximum in the $\mu$—$c$ curves is due to hydration of anions and cations as postulated above and also that this hydration effect is an additive function of the cation and anion in question, it will be easy to explain the nature of the different types of $\mu$—$c$ curves as considered above. Firstly, the alkali and ammonium salts of common inorganic acids, in general, do not show a maximum in the $\mu$-$c$ curves because the cation and anion in each case are only very slightly hydrated. A bending round in the curves of sodium and ammonium salts is indicative of a greater hydration of $Na^+$ and $NH_4^+$ ions as compared to that of $K^+$-ion. Specially notable is the case of KF ($\Delta S = -37$). A maximum in its $\mu$—$c$ curve occurs at about

35% concentration due to the $F^-$ ion being highly hydrated which makes the total entropy of KF as low as 37. On the other hand, in LiI, whose entropy value is only −29·5, the maximum should occur at a higher concentration as is suggested by its $\mu$-$c$ curve. Hence additivity of ionic hydration, in so far as its effect on $\mu$ is concerned, is very clearly brought out by these two examples.

A comparatively high hydration of $Ca^{++}$, $Sr^{++}$, $Cu^{++}$, $Mg^{++}$, $Zn^{++}$, and $Al^{+++}$ etc. brings about the maximum in the $\mu$—$c$ curves at concentrations below 30% in most cases. Here again $CdI_2$ shows an abnormality due to the very small hydration of the iodide ion ($\Delta S = -42$). It must be added, however, that the iodides of all these cations will behave similarly if their solubility allows experimental investigation. The course of the curve for $CdI_2$, however, suggests that the maximum may occur at about 60% concentration.

Min column I of Table I show that for the same anion and different cations, the maximum occurs at almost the same equivalent percentage concentration in most cases. This indicates that the cations concerned are, in general, almost equally hydrated. It must be pointed out, however, that as the maximum occurs at almost the same equivalent percentage concentration, hydration of $Li^+$ ion is about one-half of the rest. As a result of the effect of the hydration of different anions, this concentration is different for different anions *e.g.*, for chloride 0·4100, for sulphate 0·2900, and for nitrate 0·3010 approximately.

FIG. 3.



In the case of inorganic acids and chloro-substituted acetic acids it appears that the stronger the acid, the lower the equivalent percentage concentration at which the maximum occurs. Stronger acids will have a higher effective hydrogen-ion concentration and hence would involve a greater number of water molecules in the hydration process. Consequently the maximum shifts to lower concentrations due to increase in the effective mass of the ion as well as in the resistance to their movement in the medium. The anions of the acids, however, will add to this according to their hydration. In spite of the fact that various workers consider the hydrogen-ion to be least hydrated, conclusions, arrived at in this paper and supported by a number of researches, appear to show that the $H^+$ ion is sufficiently hydrated.

On the other hand in the case of aliphatic organic acids, the weaker the acid, the lower the equivalent percentage concentration at which the maximum occurs, It is likely that this behaviour is due to polymerisation of the acid molecules. The weaker the acid, the greater the polymerisation and hence lower the concentration at which the maximum is reached due to abnormal disappearance of ions from the field of action. It may be added that these polymerised molecules or 'micelles' are hydrated and this adds a great deal to the viscosity of the solutions (Tsaklotos, *Compt. rend.*, 1940, 2, 805). But probably the polymerisation of the acid molecules is the more predominant factor in these cases. We see, therefore, that it is possible to explain, in general, the nature of the specific conductivity—percentage concentration curves of solutions of electrolytes in water on the ionic hydration hypothesis as modified in the light of recent researches.

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# A VISCOMETRIC METHOD FOR STUDYING THE KINETICS OF ALCOHOLYSIS OF ESTERS

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Using a modification of Scarpa's method, satisfactory values for the unimolecular constants are obtained for the alcoholysis of methyl acetate by three alcohols in the presence of hydrochloric acid at 25° and 30°, by following the progress of the change by a determination of the viscosity of the medium. It is considered that the procedure can be of general use for a study of the kinetics of changes in liquid media.

Kinetics of alcoholysis have been studied *polarimetrically* by Patterson and Dickinson (*J. Chem. Soc.*, 1901, **79**, 280), Bruni and Contardi (*Gazzetta*, 1906, **36**, 356) and Dasannacharya (*J. Indian Inst. Sci.*, 1924, **7**, 1; *J. Amer. Chem. Soc.*, 1924, **46**, 1627); *dilatometrically* by Anderson and Holden (*J. Phys. Chem.*, 1914, **18**, 152), Kolhatker (*J. Indian Inst. Sci.*, 1915, **1**, 107) and Dasannacharya (*ibid.*, 1921, **4**, 181); *conductometrically* by Nixon and Branch (*J. Amer. Chem. Soc.*, 1936, **58**, 492, 2499). Following the work of Joshi and Raju (*Proc. Indian Sci. Cong.* 1932, *Chem. Section*, p. 193) and Joshi and Joga Rao (*ibid.*, 1933, p. 190) the kinetics of the above reaction were investigated *viscometrically*. It will be seen from a consideration of the experimental procedure detailed below that this method possesses some marked advantages over those in use hitherto, in the wider range of its applicability and the comparative simplicity of the necessary apparatus.

## EXPERIMENTAL

The general experimental arrangement was already described in detail by Joshi and Vishwanathan (*J. Indian Chem. Soc.*, 1933, **10**, 330) which is Scarpa's method (*Gazzetta*, 1910, **40**, 271; Farrow, *J. Chem. Soc.*, 1912, **101**, 347). The chief advantage here is that unlike in the case of the familiar Ostwald's method, no density measurements are required; $t_1$, the time of rise of a certain constant volume of the reaction mixture under a known suction, and $t_2$, the time of fall for the same quantity of the liquid under its own hydrostatic pressure, being all that are needed. For accuracy of measurement, constancy of the suction pressure is essential; in the present experiments it was 30±0·03 cm. of water. From a knowledge of $t_1$ and $t_2$, the viscosity, $\eta$, is given by

$$\eta = k.t_1.t_2/(t_1 + t_2)$$

where $k$ is a constant for a given viscometer and applied suction and $t_1$ and $t_2$, the times taken for the rise and fall of the liquid in the viscometer. $k$ was evaluated from observations of $t_1$ and $t_2$ at a known temperature for a standard liquid like water for which viscosity, $\eta$, is known. Two Scarpa tubes were connected suitably to the aspirator, which enabled the progress of two reactions to be followed simultaneously. The values of $k$, the viscometric constants for the two Scarpa tubes used, are 0·5537 and 0·5869.

The volume of the reaction mixture was 30 c.c. in all the cases ; it consisted of 5 c.c. of the ester, methyl acetate in the present experiments, 20 c.c. of an alcohol and 5 c.c. of the latter containing a known amount of hydrochloric acid introduced as a pure dry gas, to act as a catalyst. The various constituents of the mixture, namely the ester, the alcohol and the hydrochloric acid gas were carefully purified and freed from moisture by appropriate methods. For the actual preparation of the reaction mixture, the above amount of alcohol was kept in a tall gas jar and closed with the rubber stopper which admitted the Scarpa-tube ; this and the two other liquids contained in well stoppered bottles were allowed to attain the temperature of the thermostat, then mixed in the above gas jar and the corresponding mean time noted. Measurements of viscosity of the reacting mixture were then made at stated time intervals, for a period of 4-10 hours, depending upon the rate of the particular alcoholysis reaction. The mixture was then allowed to stand for about 24 hours, when the final reading was taken. In all cases viscosity was measured at suitable intervals for another 24 hours to ascertain the constancy of the final reading mentioned above corresponding to the end-points of the reaction. In a few cases viscosity showed a slight diminution even after the first 24 hours, and the lowest reading was taken. The reactions were studied at two temperatures, 25° and 30°, the temperature of the water in the thermostat being maintained constant within ±0·05° by employing a toluene thermoregulator and a motor driven stirrer. The unimolecular velocity constants were obtained by employing the equation,

$$k = \frac{2{\cdot}303}{t} \cdot \log_{10} \frac{a}{(a-x)}.$$

The concentration of the unchanged ester at a time $t$ was obtained on the assumption that $(a-x)$ was proportional to $(\eta_t - \eta_\infty)$. Straight lines were obtained by plotting log $(a-x)$ against $t$, in all the reactions studied. Log $a$ was then obtained from each of these lines by extrapolation to zero time. Curve B is one of such typical plot for the reaction corresponding to Table VI and curve A is another plot for the same reaction illustrating the nature of the viscosity variation of the system with time during alcoholysis (Fig. 1).

In all the experiments methyl acetate was the ester employed. Hydrochloric acid present in different concentrations served as the catalyst. Amyl, *iso*butyl and *n*-propyl alcohols were used for replacing the alkyl group in the ester. Typical experimental results obtained are shown in the following tables for the different reactions.

### TABLE I.

Conc. of catalyst = 0·1830*N*-HCl. Temp. = 30 ± 0·05°. *k* = 0·5537.
Methyl acetate + amyl alcohol + catalyst = 5, 20, 5 c.c. respectively.

| $t_1$. | $t_2$. | η. | (*a*-*x*). | log (*a*-*x*). | *t* (min.) | $k \times 10^3$. |
|---|---|---|---|---|---|---|
| | | | | log $a = \bar{1}$·1770 | 0′ by extrapolation. | |
| 6′ 18.6″ | 7′ 8·3″ | 1·855 | 0·140 | ·1461 | 17·0 | (4·15) |
| 6 16·3 | 7 6·4 | 1·843 | 0·130 | ·1139 | 35 0 | (4·15) |
| 6 15·0 | 7 3·8 | 1·835 | 0·120 | ·0792 | 55·0 | 4·10 |
| 6 12·6 | 7 1·2 | 1·824 | 0·109 | ·0374 | 80·0 | 4·03 |
| 6 9·7 | 6 58·4 | 1·810 | 0·095 | $\bar{2}$·9777 | 120·5 | 3·85 |
| 6 6·8 | 6 57·3 | 1·801 | 0·086 | ·9395 | 139·0 | 4·03 |
| 6 5·9 | 6 56·5 | 1·797 | 0·082 | ·9138 | 153·0 | 3·96 |
| 6 3·7 | 6 53·6 | 1·785 | 0·070 | ·8451 | 189·0 | 4·05 |
| 6 2·1 | 6 52·2 | 1·779 | 0·064 | ·8062 | 227 5 | 3·75 |
| 5 59·7 | 6 50·0 | 1·768 | 0·053 | ·7243 | 263·0 | 3·96 |
| 5 59·3 | 6 48·8 | 1·764 | 0·049 | ·6902 | 282 0 | 3·98 |
| 5 57·5 | 6 47 4 | 1·758 | 0·043 | ·6335 | 320·0 | 3 91 |
| 5 55·3 | 6 45·0 | 1·746 | 0·031 | ·4914 | 412·0 | 3·82 |
| 5 53·7 | 6 42·4 | 1·736 | 0 021 | ·3222 | 527 0 | 3·73 |
| 5 49·3 | 6 37·5 | 1·175 | 0 | | ∞ | |
| | | | | | | Mean 3·93 |

### TABLE II.

Conc. of catalyst = 0·1830*N*-HCl. Temp. = 25 ± 0·05°. *k* = 0·5870.
Methyl acetate + amyl alcohol + catalyst = 5, 20, 5 c.c. respectively

| $t_1$. | $t_2$. | η. | (*a*-*x*). | Log (*a*-*x*). | *t* (min ) | $k \times 10^3$. |
|---|---|---|---|---|---|---|
| | | | | log $a = \bar{1}$·2200 | 0′ by extrapolation. | |
| 6′ 17·5″ | 7′ 30·0″ | 2 008 | 0 146 | ·1644 | 24·0 | (5·24) |
| 6 16·6 | 7 28·0 | 2·002 | 0·140 | ·1461 | 54·0 | (3·16) |
| 6 17·0 | 7 26·5 | 2·000 | 0·138 | ·1399 | 71·0 | 2·60 |
| 6 13·5 | 7 25·0 | 1·985 | 0 123 | ·0899 | 108·5 | 2 74 |
| 6 13·4 | 7 23 0 | 1·983 | 0·121 | ·0823 | 125·0 | 2·53 |
| 6 10·3 | 7 20·4 | 1·969 | 0·106 | ·0253 | 167·5 | 2·67 |
| 6 10·2 | 7 19·6 | 1·966 | 0·104 | ·0170 | 189·0 | 2·46 |
| 6 7·0 | 7 17·4 | 1·952 | 0·090 | $\bar{2}$·9542 | 234·0 | 2 63 |
| 6 5·0 | 7 14·5 | 1·940 | 0·078 | ·8921 | 285·0 | 2·65 |
| 6 3·6 | 7 13·7 | 1·935 | 0·073 | ·8633 | 316 5 | 2·60 |
| 6 1·6 | 7 12·2 | 1·926 | 0·064 | ·8092 | 356·0 | 2·67 |
| 6 1 0 | 7 11·0 | 1·992 | 0·060 | ·7782 | 387·5 | 2·63 |
| 5 50·6 | 6 56·8 | 1·862 | 0·0 | | ∞ | |
| | | | | | | Mean 2·62 |

### TABLE III.

Conc. of catalyst – 0·1883$N$HCl. Temp = 25 ± 0·05°. $k$ – 0·5537.
Methyl acetate + amyl alcohol + catalyst – 5, 20, 5 c.c. respectively.

| $t_1$. | $t_2$. | $\eta$. | $(a-x)$. | $\log (a-x)$. | ($t$ min.). | $k \times 10^3$. |
|---|---|---|---|---|---|---|
| | | | | $\log a = \bar{1}$·1850 | 0·0 | |
| 6′ 19·7″ | 8′ 51·0″ | 2·043 | 0·136 | ·1335 | 28·0 | (4·24) |
| 6 19·2 | 8 50·1 | 2·040 | 0·133 | ·1239 | 45·0 | 3·13 |
| 6 18·0 | 8 48·2 | 2·032 | 0·125 | ·0969 | 72·0 | 2·81 |
| 6 14·4 | 8 44·7 | 2·015 | 0·108 | ·0334 | 113·5 | 3·09 |
| 6 11·4 | 8 40·0 | 1·990 | 0·083 | $\bar{2}$·9191 | 190·0 | 3·20 |
| 6 9·0 | 8 37·3 | 1·987 | 0·080 | ·9031 | 207·0 | 3·13 |
| 6 7·0 | 8 36·0 | 1·978 | 0·071 | ·8513 | 245·0 | 3·13 |
| 6 6·4 | 8 34·9 | 1·970 | 0·063 | ·7993 | 284·0 | 3·13 |
| 5 56·1 | 8 12·3 | 1·907 | 0 | | ∞ | |
| | | | | | | Mean 3·09 |

### TABLE IV.

Conc. of catalyst – 0·3660$N$-HCl. Temp. – 25° ± 0·05°. $k$ – 0·5537.
Methyl acetate + amyl alcohol + catalyst – 5, 20, 5 c.c. respectively.

| $t_1$. | $t_2$. | $\eta$. | $(a-x)$. | $\log (a-x)$. | ($t$ min.). | $k \times 10^3$. |
|---|---|---|---|---|---|---|
| | | | | $\log a = \bar{1}$·2750 | 0 | |
| 6′ 51·2″ | 9′ 21·0″ | 2·190 | 0·171 | ·2330 | 18·0 | 5·37 |
| 6 45·6 | 9 12·6 | 2·158 | 0·139 | ·1430 | 54·0 | 5·62 |
| 6 42·0 | 9 7·0 | 2·114 | 0·118 | ·0719 | 80·5 | 5·80 |
| 6 38·5 | 9 2·2 | 2·118 | 0·099 | $\bar{2}$·9956 | 112·0 | 5·76 |
| 6 34·0 | 8 56·3 | 2·096 | 0·077 | ·8865 | 156·0 | 5·74 |
| 6 29·0 | 8 53·3 | 2·077 | 0·058 | ·7634 | 184·0 | (6·40) |
| 6 30·0 | 8 50·0 | 2·073 | 0·054 | ·7324 | 222·0 | 5·62 |
| 6 28·4 | 8 47·4 | 2·065 | 0·046 | ·6628 | 249·0 | 5·67 |
| 6 20·0 | 8 36·8 | 2·019 | 0· | | ∞ | |
| | | | | | Mean. | 5·65 |

### TABLE V.

Conc. of catalyst = 0·1483*N*-HCl. Temp. = 30 ± 0·05°. *k* = 0·5870.
Methyl acetate + *iso*butyl alcohol + catalyst = 5,20,5 c.c. respectively.

| $t_1$. | $t_2$. | η. | $(a-x)$ | log $(a-x)$. | $t$ (min.). | $k \times 10^3$. |
|---|---|---|---|---|---|---|
| | | | | log $a = \bar{1}$·1325 | 0 | |
| 5′ 33·2″ | 6′ 25·0″ | 1·748 | 0·133 | ·1239 | 14·5 | 1·36 |
| 5 31·6 | 6 24·3 | 1·742 | 0·127 | ·1038 | 29·0 | (2·28) |
| 5 28·5 | 6 21·6 | 1·727 | 0·112 | 0492 | 74·5 | 2·58 |
| 5 27·0 | 6 18·8 | 1·718 | 0·103 | ·0128 | 122·5 | (2·26) |
| 5 24·6 | 6 17·1 | 1·706 | 0·091 | $\bar{2}$·9590 | 151·5 | 2·65 |
| 5 23·6 | 6 15·6 | 1·700 | 0·085 | 9294 | 175·0 | 2·67 |
| 5 22·2 | 6 13·5 | 1·691 | 0·076 | ·8808 | 221·5 | 2·63 |
| 5 20·6 | 6 11·8 | 1·684 | 0·069 | ·8388 | 283·5 | 2·39 |
| 5 19·0 | 6 10·0 | 1·676 | 0·061 | ·7853 | 320·0 | 2·51 |
| 5 17·4 | 6 9·5 | 1·670 | 0·055 | ·7404 | 347·5 | 2·60 |
| 5 15·0 | 6 7·8 | 1·661 | 0·046 | ·6628 | 387·0 | 2·79 |
| 5 15·0 | 6 6·8 | 1·658 | 0·043 | ·6335 | 423·5 | 2·72 |
| 5 14·3 | 6 5·8 | 1·654 | 0·039 | ·5911 | 466·5 | 2·67 |
| 5 12·8 | 6 4·6 | 1·647 | 0·032 | ·5051 | 510·0 | 2·83 |
| 5 11·2 | 6 3·6 | 1·641 | 0·026 | ·4150 | 609·0 | 2·72 |
| 5 7·9 | 5 57·5 | 1·615 | 0· | | ∞ | |
| | | | | | Mean | 2·65 |

### TABLE VI.

Conc. of catalyst = 0·1483*N*-HCl. Temp. = 25 ± 0·05°. *k* = 0·5537.
Methyl acetate + *iso*butyl alcohol + catalyst = 5, 20, 5 c.c. respectively.

| $t_1$. | $t_2$. | η. | $(a-x)$. | log $(a-x)$. | $t$ (min.). | $k \times 10^3$. |
|---|---|---|---|---|---|---|
| | | | | log $a = \bar{1}$·1265 | | |
| 5′ 40·6″ | 7′ 50·2″ | 1·823 | 0·136 | ·1335 | 12·0 | |
| 5 39·0 | 7 49·0 | 1·816 | 0·129 | ·1106 | 27·0 | 1·36 |
| 5 38·4 | 7 48·2 | 1·813 | 0·126 | ·1004 | 45·0 | 1·34 |
| 5 37·8 | 7 46·8 | 1·808 | 0·121 | ·0828 | 75·0 | 1·34 |
| 5 36·0 | 7 46·0 | 1·801 | 0·114 | ·0569 | 120·0 | 1·34 |
| 5 35·0 | 7 44·6 | 1·796 | 0·109 | ·0374 | 153·0 | 1·34 |
| 5 34·0 | 7 42·4 | 1·789 | 0·102 | ·0086 | 204·4 | 1·33 |
| 5 33·0 | 7 41·0 | 1·783 | 0·096 | $\bar{2}$·9820 | 250·0 | 1·33 |
| 15·4 | 7 14·8 | 1·687 | 0 | | ∞ | |
| | | | | | Mean | 1·84 |

TABLE VII.

Conc. of catalyst = 0·2*N*-HCl. Temp. – 30 ± 0·05°. $k = 0·5537$.
Methyl acetate + *n*-propyl alcohol + *n*-catalyst – 5, 20, 5 c.c. respectively.

| $t_1$. | | $t$. | | $\eta$. | $(a-x)$. | $\log (a-x)$. | $t$ (min.). | $k \times 10^3$. |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $\log a = \bar{2}$·8200 | 0 | |
| 4′ | 59·2″ | 6′ | 48·6″ | 1·593 | 0·061 | ·7853 | 21·0 | 3·80 |
| 4 | 56·5 | 6 | 46·6 | 1·582 | 0·050 | ·6990 | 80·0 | 3·48 |
| 4 | 56·0 | 6 | 45·2 | 1·578 | 0·046 | ·6628 | 109·5 | 3·32 |
| 4 | 54·7 | 6 | 44·0 | 1·572 | 0·040 | ·6021 | 144·5 | 3·48 |
| 4 | 53·2 | 6 | 42·9 | 1·565 | 0·033 | ·5185 | 195·5 | 3·55 |
| 4 | 53·0 | 6 | 41·6 | 1·563 | 0·031 | ·4914 | 220·0 | 3·45 |
| 4 | 51·4 | 6 | 41·4 | 1·557 | 0·025 | ·3979 | 241·5 | 4·03 |
| 4 | 51·2 | 6 | 41·3 | 1·557 | 0·025 | ·3979 | 255·5 | 3·80 |
| 4 | 50·6 | 6 | 38·4 | 1·552 | 0·020 | ·3010 | 303·5 | 3·94 |
| 4 | 48·6 | 6 | 37·8 | 1·543 | 0·011 | ·0414 | 340·0 | (5·27) |
| 4 | 48·5 | 6 | 36·5 | 1·541 | 0·009 | $\bar{3}$·9542 | 374·0 | (5·34) |
| 4 | 46·6 | 6 | 34·0 | 1·532 | 0 | | ∝ | |
| | | | | | | | Mean | 3·65 |

## DISCUSSION

After the intermediate complex-formation theory for esterification reactions demonstrated by Goldschmidt and co-workers in a series of papers (*Z. physikal. Chem.*, 1907, **60**, 728; 1912, **81**, 30; 1929, **143**, 139, 278), the mechanism of acid-catalysed alcoholysis reactions may be represented as comprising initially the formation of complexes of the H-ions from the catalyst with the alcohol molecules, the interchange of the alkyl group in the ester taking place subsequently by the interaction between these complexes and the ester under test. The alcoholysis of methyl acetate may therefore be represented as follows:—

$$R_x\,OH + H^+ (\text{from HCl acid}) \longrightarrow R_x\,OH_2^+ \quad .. \quad (i)$$

$$CH_3{\cdot}COOC_2H_5 + R_xOH_2^+ \longrightarrow R_x{\cdot}COOC_2H_5 + \underset{\displaystyle CH_3OH + H^+ (\text{catalyst})}{\underset{\downarrow}{CH_3OH_2^+}} \quad (ii)$$

Where $R_x$ is the alkyl group which is sought to interchange with the methyl group of methyl acetate. The rate of alcoholysis may be expressed by the equation,

$$\frac{d\,(R_x{\cdot}COOC_2H_5)}{dt} = k\,(CH_3{\cdot}\,COOC_2H_5)(R_x.\,OH_2^+).$$

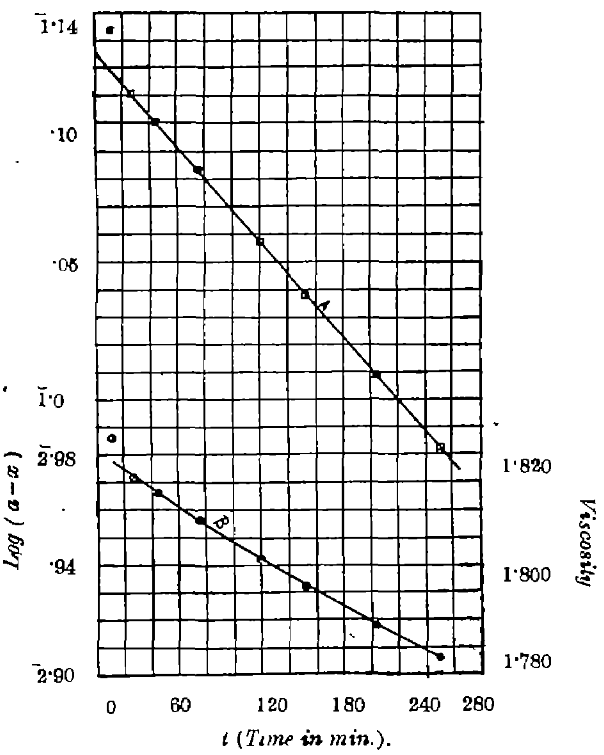
As, however, the alcohol $R_xOH$ was maintained to be present in great excess in all the reactions studied, its concentration and therefore its active mass may be taken to remain practically constant throughout the reaction, and the equation reduces to one of the first order. The velocity constant, $k$, is then given by,

$$k = \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a-x}.$$

This is in satisfactory agreement with the experimental results as can be seen from the concordant values of $k$, given in the last column of the above tables.

From curve A (Fig. 1) and from the viscocity data given in column 3 in the tables, it is clear that the variation in viscosity of the reacting mixture during the progress of alcoholysis is appreciable enough in magnitude to be easily measured by the present experimental method, and to enable the velocity constants to be computed by applying the appropriate law for the particular reaction. It is thus seen that measurement of viscosity variations with time employing a Scarpa's type of viscometer, constitutes a very simple method of studying the kinetics of alcoholysis of esters.

FIG 1.



The effect of increasing the strength of the catalyst, keeping other things the same, is shown in Tables II, III and IV. The mean values of $k$, obtained therein, are seen to be directly proportional to the concentrations of the hydrochloric acid employed as catalyst. This is in agreement with a similar experimental finding of Kolhatker (*loc. cit.*) for the alcoholysis of *iso*butyl acetate in presence of methyl alcohol, catalysed by HCl acid. This is expected to be so, since in dry alcohol the concentration of alcohol-complex may be considered to be equal to the total $H^{\cdot}$ concentratration, or in this case, where a strong mineral acid is used, to the concentration of such acid.

The influence of temperature on the reaction velocity is seen in the values of the velocity constants obtained at 25° and 30°. The values of the velocity constants are nearly doubled by 5° rise in temperature (*i.e.*) from 25° to 30°. It was intended to continue this work with a view to obtaining the velocity constants at two or three other temperatures and evaluate the activation energies.

In conclusion the author desires to express his sincere thanks to Dr. S. S. Joshi, Principal of the College of Science, Benares Hindu University, for suggesting the problem, and for facilities offered for conducting this work.

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# KINETICS OF OXIDATION OF SOIL ORGANIC MATTER. PART I. RELATIVE ORDERS OF OXIDATION WITH SOME CHEMICAL REAGENTS

By S. P. Roychoudhuri and A. B. Bhuiyan

The relative order of the rates of oxidation of soil organic matter of seveal soil samples and of Merck's humic acid have been carried out with (*a*) alkaline and acid potassium permanganate solutions and (*b*) acid potassium dichromate solution. The relative order with all the samples by these oxidants are similar.

The oxidation of soil organic matter may be effected by chemical reagents like acid and alkaline potassium permanganate, acid potassium dichromate and and hydrogen peroxide. The oxidation of solid by a liquid oxidant is a case of heterogeneous reaction and, therefore, the theoretical considerations of homegeneous reactions are inapplicable to such cases. If, however, there be any inherent difference in the nature of the organic matter, it will be brought out in oxidation curves.

Robinson (*J. Agric. Res.*, 1927, **34**, 339), Wakemnn and Stevens (*Soil Sci.*, 1930, **30**, 97) and others have treated soils with varying concentrarions of hydrogen peroxide to determine their humus contents. Esh and Guha-Sircar (*J. Indian Chem. Soc.*, 1940, **17**, 405) have studied the conditions under which soil humus can most easily be oxidised by hydrogen peroxide. In our present experiments, however, hydrogen peroxide was found not to be a suitable oxidising reagent for measuring the rate of oxidation of the organic matter, since it is easily decomposed by the walls of the containing vessel and by the powdered materials of the soil. Under such conditions, although by blank experiments, some correction of the disturbances due to the solid particles may be effected, any quantitative conclusions drawn from those data on the nature of the organic matter of the soil, will not be beyond criticism. Besides, the decomposition of hydrogen peroxide itself will be considerably affected by slight changes of temperature.

In the present paper, the rates of oxidation of the organic matter of eight top soil samples by the following chemical reagents have been determined: ( alkaline potassium permanganate solution ( 0·1052 *N*), (*ii*) acid potassiam permanganate solution ( 0·1052 *N*) and (*iii*) acid potassium dichromate solution ( 0·111 *N*).

These studies were also carried out with Merck's humic acid and with Dacca soil in which no manure was added, and the same soil treatment with green manure alone, and after combined treatments with green manure and lime, as also with green manure and lime and bone dust.

## EXPERIMENTAL

Organic carbon in the soils was determined by following the rapid titration procedure advised by Walkley (*J. Agric. Sci.*, 1935, **25**, 598) and total nitrogen of the samples were determined by Kjeldahl's method. The results are shown in Table I.

TABLE I.

*Percentages of organic carbon in the samples.*

| Substance. | Locality. | Organic carbon. | Nitrogen. | C/N ratio. |
|---|---|---|---|---|
| Dacca soil + no manure * | Dacca | 0·63% | 0·0501% | 12·60 |
| Dacca soil + green manure * | „ | 1·50 | 0·057 | 26·31 |
| Dacca soil + green manure + lime * | „ | 0·60 | 0·056 | 10·71 |
| Dacca soil + green manure + lime + bone dust * | „ | 1·30 | 0·060 | 20·66 |
| Soil No 24A * * | Raipur C. P. | 0·714 | 0·0602 | 11·9 |
| „ „ 30A * * | Teliparamba Madras | 5·68 | 0·35 | 16·02 |
| „ „ 34A * * | Calicut Madras | 1·653 | 0·146 | 11·32 |
| „ „ 64 * * | Tenasserim Burma | 2·857 | 0·166 | 17·2 |
| „ „ 80 * * | Satgaon Assam | 1·418 | 0·13 | 10·09 |
| „ „ 98A * * | North Haji, Dacca Farm | 0·99 | 0·087 | 11·38 |
| „ „ 184 P * * | Coimbatore | 0·810 | 0·055 | 14 72 |
| „ „ 186 P * * | Coimbatore | 0·410 | 0 040 | 10·25 |
| Humic acid (Merck's) | ... | 43·0 | 2·94 | 14·62 |

* These samples were kindly supplied by Dr. S. S. Guha-Sircar.

** Laboratory Number

## *Rates of the Oxidation.*

The soils were finely powdered and passed through a 100 mesh sieve. Calculated quantities of soils containing 0 02g. of organic carbon were taken in 150 c. c. stoppered glass bottes and mixed with 100 c. c. of the oxidising reagents at a known instant of time. The bottles were then fixed to the clamps on the disc rotating inside a thermostat (25±02°). The exact time at which the contents of each of the bottles were mixed were noted. At suitable intervals of time, the bottles were, in order, released from the clamps and placed for settling on a stand immersed in the water of the thermostat. At known instants of time, the clear supernatant liquids were pipetted out of the bottles and the amounts of oxidants present in the filtrates were determined by titrating with a suitable titrating liquid. In the case of alkaline potassium permanganate solution, the precipitated manganese dioxide was effectively removed by filtering the pipetted solution through a No. 3 sintered glass filter.

The oxidation curves with one of the three oxidising agents are shown in Fig. 1, while Table II summarises the relative orders of oxidation. The relative orders of the percentage of organic matter in different samples (*cf.* Table I) were also included in the same table.

FIG. 1.

*Oxidation with acid* $KMnO_4$.

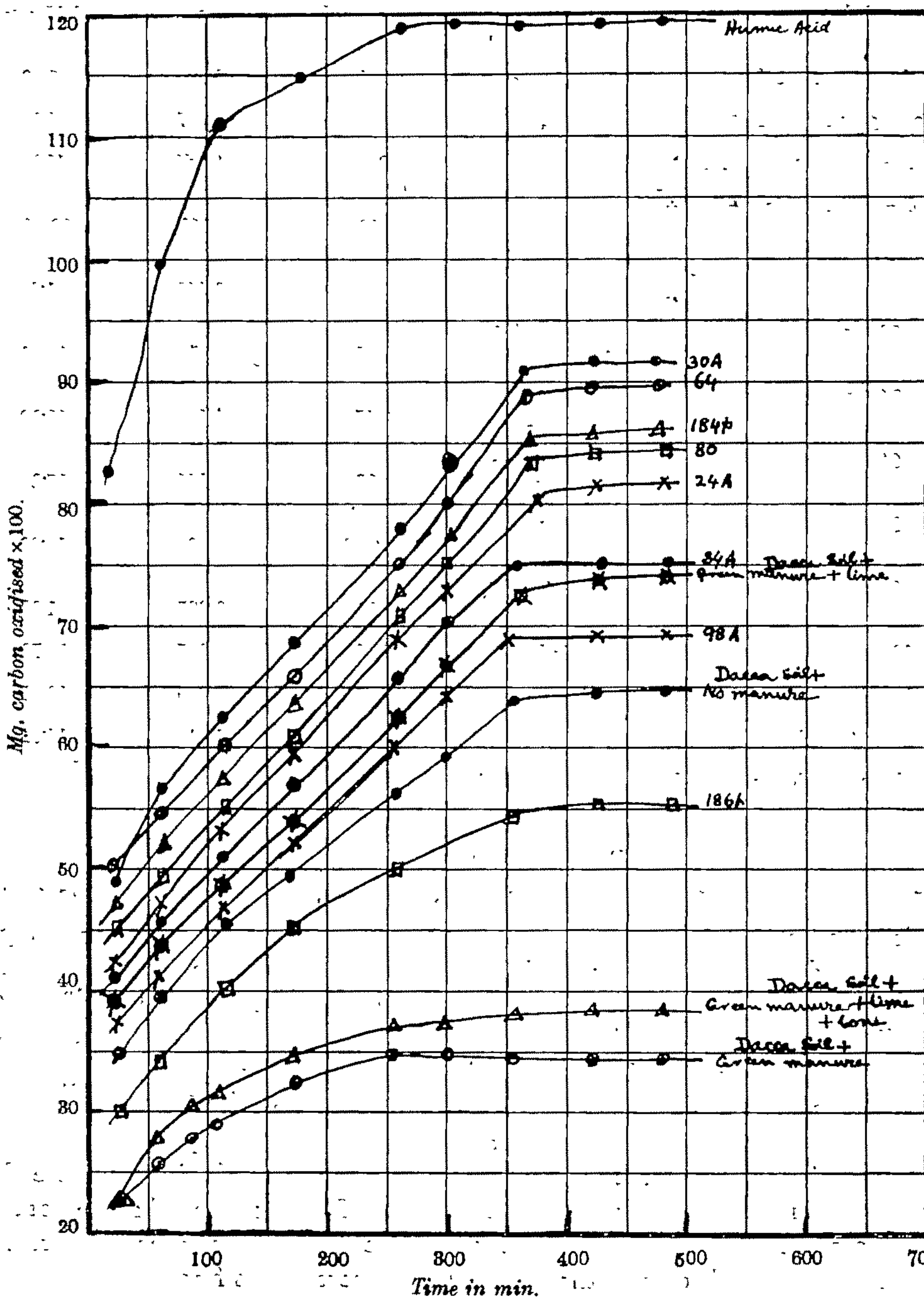

TABLE II.

*Order of oxidation.*

| Alkaline $KMnO_4$. | Acid $KMnO_4$. | Acid $K_2Cr_2O_7$. | Percentage of organic matter in different samples. |
|---|---|---|---|
| Humic acid> 30A> 64> 24A> 80> 98A> green manure+lime (Dacca soil)> 34A> no manure (Dacca soil)>186 P> 184 P> green manure+lime+bone (Dacca soil)> green manure (Dacca soil). | Humic acid> 30A> 64> 184 P> 80> 24A> 34A> green manure+lime (Dacca soil)> 98A> no manure (Dacca soil)> 186 P> green manure+lime+bone (Dacca soil)> green manure (Dacca soil). | Humic acid> 30A> 64> 24A> 98A> green manure+lime (Dacca soil)> no manure (Dacca soil)> 186 P> 80> 184 P> 24A> green manure+lime+bone (Dacca soil)> green manure (Dacca soil). | Humic acid> 30A> 64> 34A> green manure (Dacca soil) 80> green manure+lime+bone (Dacca soil)>98A> 184P> 24A> no manure (Dacca soil) green manure+lime(Dacca soil)> 186 P. |

The rates of oxidation of the samples by three reagents are similiar. This order is also more or less similar to that organic matter contents of the soils when we leave out the green manuring treatments. The results indicate that, at least partially, the ratios of soil solutions are determininig the rates of oxidation of organic matters in soils, as the soils taken in these experiments are in inverse propotion to their organic carbon contents.

It was found that in the initial stages the rate of oxidation of the organic carbon of the soil, which is quite high, gradually decreases with time and after about six hours the amount of organic carbon oxidised reaches a maximum value. With humic acid it was found that after about two to three hours, the amount oxidised by the chemical reagents reaches a maximum value and that acid potassium permanganate oxidises it to a much greater extent than any of the other two chemical reagents. It was found that although the amount of humic acid used in these experiments contained 20 mg. of organic carbon, the actual amounts of organic carbon oxidised vary from 0·5 mg. to 1·2 mg. This suggests, therefore, that Merck's humic acid consists mostly of highly resistant type of organic matter. The same is true with the organic matter of soils.

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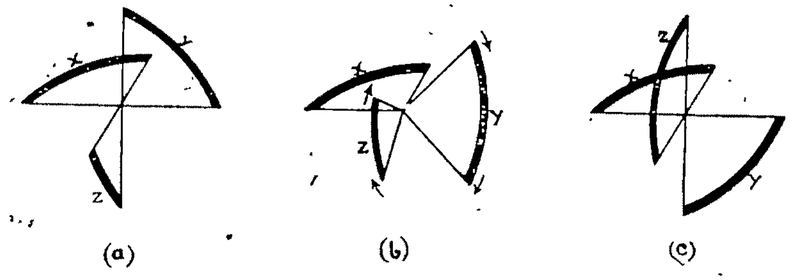
# KINETICS AND MECHANISM OF RACEMISATION OF OPTICALLY ACTIVE COBALTIC *TRIS*BIGUANIDE COMPLEX

By Priyadaranjan Rây and Nihar Kumar Dutt

The velocity of racemisation of $l$- and $d$-cobaltic *tris*biguanidinium chloro-$d$-tartrate, as well as of the pure optical enantiomers, $l$- and $d$-cobaltic *tris*biguanidinium chloride, in aqueous solution have been determined at different temperatures. The activation energy in each case has been computed from the temperature coefficient of the velocity constant of inversion with the help of Arrhenius's equation. In the case of the pure enantiomers the value for the Arrhenius's constant $PZ$) was found to be very low from the point of view of the unimolecular type of change. Addition of many simple and complex foreign cations, including H-ion, has been found to retard catalytically the velocity of racemisation of the active cobaltic *tris*biguanidinium chloride. $Ca^{++}$, $Cu^{++}$, $Mn^{++}$ and $H^+$ are most effective in this respect and almost completely inhibit the change even when present in very small quantities. The change is, however, unaffected by anions excepting the OH-ion, which exercises, on the other hand, a strong accelerating effect upon the velocity of racemisation. The existing views regarding the mechanism of racemisation have been discussed in the light of experimental results described in this paper, as well as of those previously recorded by others. A new mechanism of the phenomenon of racemisation has been suggested on the basis of intramolecular rearrangement.

The phenomenon of racemisation of optically active co-ordination compounds has lately become a subject of special interest for investigation. The mechanism of racemisation implies that of inversion till the two optically active antipodes are present in equal amounts in dynamic equilibrium. Two main views have been advanced relating to this phenomenon. The one, due to Werner (*Ber.*, 1912, **45**, 3061), is based on the *intramolecular rearrangement* of the co-ordinated bidentate groups. Thus in the case of active potassium cobalti- or chromioxalate none of the three oxalato groups are entirely detached from the central atom, only one of them vacates momentarily one of its two co-ordination positions in the molecule remaining bound at the other position, and before it can rejoin a rearrangement with one of the other oxalate groups occurs, leading to the formation of its enantiomorph (Fig. 1*a* and *c*).

Fig. 1



Thomas (*J. Chem. Soc.*, 1921, **119**, 1140), on the other hand, considers *secondary ionisation* as the cause of racemisation. He assumes that potassium chromi- or cobaltioxalate, for instance, in aqueous solution suffers partial dissociation, as shown below, giving rise to a planar complex,

$$d\text{- or } l\text{- } [M(C_2O_4)_3]^{3-} \rightleftharpoons \underset{\text{planar}}{[M(C_2O_4)_2]^-} + (C_2O_4)^{=}.$$

Subsequent recombination leads to racemisation, due to equal probability for the formation of both the enantiomers.

Thomas's view has been criticised by Johnson and co-workers (Johnson, *Trans. Faraday Soc.*, 1935, **31**, 1615; Beese and Johnson, *ibid.*, 1635; Bushra and Johnson, *J. Chem. Soc.*, 1939, 1941), who could not detect the presence of any free ($C_2O_4$)-ion in the solution of chromi- or cobaltioxalate, nor did they observe any reduction in the rate of racemisation of these active substances by the addition of potassium oxalate (common ion effect). Furthermore, both chromioxalate and cobaltioxalate have been found to racemise even in the crystalline state (Johnson and Mead, *Trans. Faraday Soc.*, 1935, **31**, 1621, Johnson, *ibid.*, 1620). Finally Long (*J. Amer. Chem. Soc.*, 1939, **61**, 570) has failed to detect any exchange between oxalate ion containing a radioactive isotope of carbon with chromioxalate at 35°.

Johnson and collaborators are, therefore, in favour of the alternative view of racemisation through intramolecular rearrangement, due to an interchange of two points of attachment in *cis*-positions (Fig. 1*a* and *c*). But they at the same time assume further that water molecules, from the solvent or water of crystallisation, possibly participate in the process (*cf.* Charonnat, *Ann. Chim.*, 1931, **16**, 150); for, they have observed that hydrated potassium chromioxalate racemises faster at room temperature than at 115°, while its strychnine salt (also hydrated) does not racemise at ordinary temperature, but racemisation occurs on heating as well as at the room temperature in the anhydrous state (dried over $P_2O_5$). These authors have also studied the kinetics of racemisation of $[Cr(C_2O_4)_3]^{3-}$, $[Co(C_2O_4)_3]^{3-}$ and $[Cr.en(C_2O_4)_2]^{-}$ in aqueous solution, and, in addition, the catalytic (accelerating) influence of foreign ions upon the velocity of their inversion (en = ethylenediamine).

These oxalato-complexes in aqueous solution are thermodynamically and otherwise rather unstable, and cobaltioxalate is moreover known to be highly sensitive to light. It was, therefore, expected that the study of an energetically stable, but optically unstable, compound might furnish more useful information on the subject. A suitable substance with these properties has been found in cobaltic *tris*biguanidinium chloride, whose resolution and optical properties have been described in our previous paper (*J. Indian Chem. Soc.*, 1941, **18**, 289). A study of the velocity of racemisation in aqueous solution of the diastereoisomerides—the chloro-*d*-tartrates of the *d*- and the *l*-complex, as well as of the complex enantiomers, *d*- and *l*-$[Co(BigH^+)_3]Cl_3$, at various temperatures and in the presence of a number of foreign ions is presented in this paper. From a consideration of the results obtained, the nature of the mechanism of racemisation has been discussed at the end.

## RESULTS AND DISCUSSION

The complex *tris*biguanidinium ion, $[Co(BigH^+)_3]^{3+}$, where BigH = $C_2N_5H_7$(biguanide), in aqueous solution is quite stable. A solution of the complex chloride can be heated to boiling without any appreciable permanent change. This does not, of course, exclude any hydrolytic equilibrium in solution on heating. In fact, evidence for such equilibrium has been discussed hereafter. Its optically active components in the solid state retain their activity unchanged even after a year; in solution their activity suffers no change at room temperature (25°) for over 24 hours. The crystals of the diastereoisomerides as well as of the active chlorides can be heated to 105° without any loss of their activity, the hydrated crystals of the former, however, became anhydrous at 62° (*cf.* Rây and Dutt, *loc. cit.*).

All measurements of rotation were made with aqueous solutions of the active salts in a Schmidt and Haensch's polarimeter provided with an electrically controlled thermostat (±1°), using a sodium vapour lamp as the light source The velocity constant of inversion for the active complex ion is deduced from the equation, $dx/dt = k(a-x) - kx = k(a-2x)$,

where $a$ = initial concentration of the active salt, $x$ = concentration of its optical antipode formed by inversion after a time $t$, and $k$ = velocity constant of inversion of the active forms. Hence,

$$k = \frac{2{\cdot}303}{2t} \log_{10} \frac{R_0}{R_t} \text{ and } T \text{ (half-life)} = \frac{2{\cdot}303}{2k} \log_{10} 2 \text{ ; where } R_0 = \text{ initial rotation, } R_t =$$

rotation after a time $t$ in minutes. From a number of pairs of polarimeter readings at each temperature the values for the unimolecular velocity constant of inversion were calculated and $k$ represents the mean of several such closely agreeing values. No anomaly in the $k$-value was observed during the entire course of the experiments, which usually lasted for several hours and sometimes even for days, unlike those found by Johnson and co-workers for chromioxalates.

Of the two diastereoisomerides, *l*- and *d*-*tris*biguanidinium chloro-*d*-tartrate, the *l*-modification can be obtained easily in a quite pure state (*cf.* Rây and Dutt, *loc. cit.*). This was, therefore, employed for measuring their rates of racemisation, specially in view of the fact, described hereafter, that the presence of small quantities of foreign ions exerts a pronounced catalytic effect upon the racemisation velocity.

The unimolecular velocity constant $k_1$ and $k_2$ for the *l*- and the *d*-diastereoisomerides respectively were calculated from

$$k_1 + k_2 = \frac{2{\cdot}303}{t} \cdot \log_{10} \frac{K}{K - (K+1)\dfrac{x}{a}} = \frac{2{\cdot}303}{t} \log_{10} \frac{K}{K - (K+1)\dfrac{R_0 - R_t}{2R_0}}$$

where $K$ = equilibrium constant for the two diastereoisomerides $= k_1/k_2$ and $a$, $x$, $t$, $R_0$ and $R_t$ denote values as already stated.

The value of $K$ for 45·1° is 1·049 and the values for other temperatures were computed from the heat of reaction 923 calories involved in the transformation of *l*- into *d*-form (*cf.* Rây and Dutt, *loc. cit.*).

### *The Velocity Constant of Inversion of the Diastereoisomerides* l- and d-$[Co(BigH^+)_3]\genfrac{}{}{0pt}{}{Cl}{d\text{-}C_4H_4O_6}$ *and their Temperature Coefficients*

The preparation and the properties of the diastereoisomerides have been described in our previous paper. All measurements were made with 1% solution in a 10 cm. tube, the rotations $\alpha_D$, the velocity constants and the half-life period, $T$, are shown in Table I.

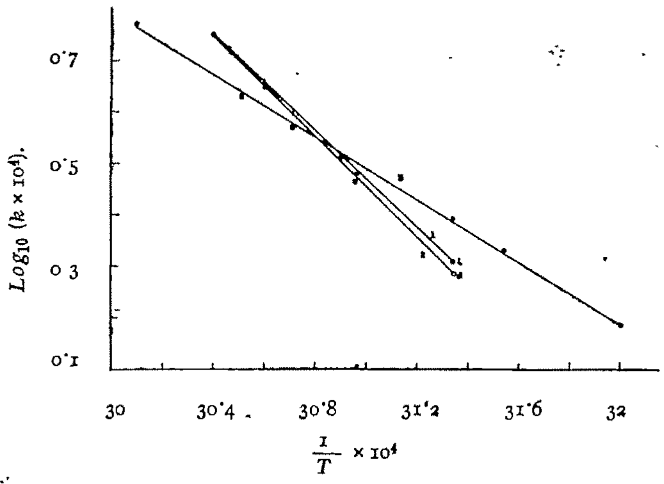
It will be observed, as could be expected from the variation of equilibrium constant with temperature (Rây and Dutt, *loc. cit.*), that the velocity constants of the two diastereoisomerides approach each other closely with rise of temperature and become practically identical above 56°. The partial racemate at about this temperature will consequently consist of 50-50 mixture of the two active forms. The phenomenon of asymmetric transformation described in our previous paper cannot, therefore, occur here.

TABLE I

| | | | | | $k_1 \times 10^4$ | $k_2 \times 10^4$ | $T_1$(hrs.) | $T_2$(hrs.) |
|---|---|---|---|---|---|---|---|---|
| Temp. = 46·1° | | | | | | | | |
| $t$ (min.) | 0 | 1020 | 1500 | 2460 | | | | |
| $\alpha_D$ (deg.) | 3·35 | 2·20 | 1·80 | 1·20 | 2·052 | 1·955 | 28·15 | 29·55 |
| Temp. = 50·2° | | | | | | | | |
| $t$ | 0 | 240 | 480 | 1440 | | | | |
| $\alpha_D$ | 3·35 | 2·90 | 2·50 | 1·38 | 3·031 | 2·942 | 19·07 | 19·65 |
| Temp. = 54·2° | | | | | | | | |
| $t$ | 0 | 180 | 420 | 1380 | | | | |
| $\alpha_D$ | 3·35 | 2·84 | 2·28 | 0·95 | 4·565 | 4·507 | 12·65 | 12·80 |
| Temp. = 56·1° | | | | | | | | |
| $t$ | 0 | 180 | 420 | 1380 | | | | |
| $\alpha_D$ | 3·35 | 2·73 | 2·09 | 0·71 | 5·630 | 5·610 | 10·27 | 10·30 |

By plotting the values of $\log_{10} k_1$ and $\log_{10} k_2$ against the reciprocal of absolute temperatures (Fig. 2, curves 1 and 2), the activation energy of the two modifications were calculated with the application of Arrhenius's equation, $k = se^{-E/RT}$. The values found for $E_l$ and $E_d$ are 21,350 cals. and 22,310 cals. respectively. The straight lines representing the relationship between log $k_1$ and log $k_2$ with temperature seem to cross each other at 56°. The solution in equilibrium at any temperature above 56° will, therefore, show a residual *laevo* rotation. Unfortunately, however, the complex ion in solution gives indication of incipient hydrolysis on keeping for about an hour at 61°, or for several hours at 59° (*vide infra*), rendering any prolonged measurements for equilibrium beyond 56° of little value.

Fig. 2



The difference between $E_l$ and $E_d$, 22,310 − 21,350 = 960 cals. is the heat evolved in the transformation of the *l*- into *d*-form, which agrees fairly well with the value of 923 cals., previously determined from equilibrium consideration (Rây and Dutt, *loc. cit.*). The values for Arrhenius's constant, $s = PZ$, calculated from the activation energy figures, are $10^{9 \cdot 14}$ and $10^{9 \cdot 8}$ for the *l*- and the *d*-variety respectively, when the velocity constants are expressed in reciprocal seconds.

## *Velocity Constants of Inversion of* l- *and* d-$[\mathrm{Co(BigH^{4})_3}]\,\mathrm{Cl_3}$ *and their Temperature Coefficients*

The preparation of the pure enantiomers has been described in our previous paper (*loc. cit.*). Most of the measurements in this paper were carried out with the *l*-isomer, which is more easily prepared.

The velocity constants for *l*-complex measured for different concentrations at 46·1°, are given in Table II.

TABLE II

| | | | | | |
|---|---|---|---|---|---|
| Conc (mols/litre) × $10^3$ ... | 10·67 | 21·34 | 42·71 | 63·76 | 85·25 |
| $k \times 10^4$ ... | 2·46 | 2·51 | 2·49 | 2·46 | 2·50 |
| ,, (mean) ... | 2·48 | | | | |

For the dextro-isomeride at the same temperature for a concentration, $c \times 10^3 = 42·68$, the value of $k \times 10^4$ was found to be 2·46.

The results show that, within the limits of the concentration employed, the transformation is strictly of the unimolecular type.

For the measurement of temperature coefficient a 3 % solution of the *laevo*-salt in 2 cm. tubes was used. The results are summarised in Table III.

TABLE III

| Temp. | ... | 39·5 | 44·1 | 46·1 | 48·2 | 50·7 | 52·7 | 54·8 | 57·1 | 59·2 |
|---|---|---|---|---|---|---|---|---|---|---|
| $k \times 10^4$ | ... | 1·52 | 2·14 | 2·46 | 2.82 | 3·24 | 3·72 | 4·28 | 4·94 | 5·84 |
| $T$ (hours) | .. | 38·2 | 27·0 | 23·5 | 20·5 | 17·8 | 15·5 | 13·5 | 11·7 | 10·3 |

Calculated from the slope of the $\log_{10} k - T^{-1}$ curve (Fig 2, curve 3) with the help of Arrhenius's equation the activation energy $E$ equals 13,930 cals and $\log_{10} PZ$ equals 4·16 on the basis of $k$ expressed in $\sec^{-1}$. As reflected in its lower activation energy the temperature coefficient of increase of the inversion constant of the active $[Co(BigH^+)_3]Cl_3$ is smaller than that of its diastereoisomerides, though the magnitude of the $k$-value for the former at lower temperatures is actually higher (*e.g.* at 46·1° these are 2·46, 2·052 and 1·955 resp.). The situation is, however, reversed at somewhat higher temperatures. In view of the lower activation energy of the active complex chloride, compared with those of its diastereoisomerides, a much higher value for its rate of racemisation than actually observed might have been expected. This is obviously offset by a rather abnormally low value of $PZ$. Similar low $PZ$-values have also been reported for the active anion $[Cr(C_2O_4)_3]^{3-}$ by Bushra and Johnson (*loc. cit.*) ; $\log_{10} PZ$ for which should be 6·2 in place of 8·05 when $k$ is expressed in $\sec^{-1}$. An increase of activation energy for the diastereoisomerides is accompanied by an increase of $PZ$-values. A similar relation has been observed by Fairclough and Hinshelwood for some bimolecular reactions (*J. Chem. Soc.*, 1937, 538). The theoretical interpretation of such relationship has been discussed by Hinshelwood (*ibid.*, 1935, 1114). But the value of 4·16 in the present case is rather unusually low for a unimolecular reaction. It may, therefore, be suggested that the water molecules as solvent are possibly not inert, but exercise their influence by modifying the rate of activation and deactivation, or by altering the number of internal degrees of freedom of the molecule (*cf.* Moelwyn Hughes, "The Kinetics of Reactions in Solutions," 1933, p. 158). The former is rather improbable for a complicated molecule like the present one, and the latter contributes only to the energy of activation. It is more likely, however, that the low value of $PZ$, or rather of the probability factor $P$, is due to an unusual delay in the specific energy transfer, which means an increase in the time-interval between *pre-activation* and *critical activation*, with the result that most of the activated molecules suffer deactivation before the transformation sets in.

At 59·2°, after a period of 12-14 hours it was found that the $k$-value went on increasing. After 24 hours it became $7·23 \times 10^{-4}$. At 61° this abnormal behaviour of the solution was more pronounced, as is evident from the following $\alpha_D$- and $k$-values of a 2% solution of the active salt in a 2 cm. tube (Table IV).

TABLE IV

| $t$ (min.) | ... | 0 | 60 | 180 | 360 |
|---|---|---|---|---|---|
| $\alpha_D$ | ... | 1·81 | 1·65 | 1·34 | 0·70 |
| $k \times 10^4$ | ... | | 7·70 | 8·35 | 13·20 |

The solution had a $p_H$ of 8·45 to begin with, which changed to 6·52 after the experiment. A hydrolytic reaction leading to the formation of a hydroxo-aquo complex as in the case of the corresponding chromium compound (Rây and Saha, *J. Indian Chem. Soc.*, 1938, **15**, 353; Rây and Ghosh, *ibid.*, 1942, **19**, 1) possibly becomes prominent at this temperature.

## *Influence of Foreign Ions on the Velocity of Racemisation*

### A. *Cations*

The higher values of activation energy of the diastereoisomerides seem to suggest their greater stability compared to that of the active complex chlorides. That combination with an active optically stable ion of opposite character imparts greater stability to an active optically unstable ion, is a phenomenon of general occurrence. This, along with the observation that unimolecular reactions are usually sensitive to homogeneous catalysis, led us to study the influence of foreign ions on the velocity of racemisation of active $[Co(BigH^+)_3]Cl_3$. Johnson and co-workers (*loc. cit.*) have already observed an accelerating effect of cations on the racemisation velocity of $[Cr(C_2O_4)_3]^{3-}$, $[Cr\ en(C_2O_4)_2]^-$ and $[Co(C_2O_4)_3]^{3-}$. Our results, on the contrary, show a catalytic retardation in all cases excepting that of OH-ion. The experimental results are summarised in the following tables. All measurements were made at 46·1° with 2% ($4·3 \times 10^{-2}$ mols/litre) solution of the *l*-hydrochloride in 2 cm. tubes

TABLE V

Catalyst—H-ion (HCl)

| Conc. of catalyst (mols./litre) | $k \times 10^5$ | Conc of catalyst (mols/litre) | $k \times 10^5$ |
|---|---|---|---|
| $1 \times 10^{-1}$ | Decomposes | $2·5 \times 10^{-4}$ | 4·04 |
| $5 \times 10^{-2}$ | 2890 | $1·0 \times 10^{-4}$ | No change for over 27 hrs. |
| $1 \times 10^{-2}$ | 545 | $0·8 \times 10^{-4}$ | 11·80 |
| $1 \times 10^{-3}$ | 206 | $0·7 \times 10^{-4}$ | 16·40 |
| $6·7 \times 10^{-4}$ | 24·90 | $0·625 \times 10^{-4}$ | 18·80 |
| $5 \times 10^{-4}$ | 13·70 | $0·5 \times 10^{-4}$ | 24·60 |

The results are represented graphically by plotting the logarithm of the concentration against $\log_{10}k$ in Fig. 3.

From an examination of Table V and Fig. 3, it will be observed that the catalytic effect of H-ion varies according to its concentration apparently in an irregular manner At $0·5 \times 10^{-4}$ molar, no catalytic effect is noticeable, beyond this up to a concentration of $0·8 \times 10^{-4}$ molar the $k$-value continually diminishes, this retardation effect reaches its maximum at $1 \times 10^{-4}$ molar when the rotation of the solution was found to remain unchanged for over 27 hours. The substance can thus be optically stabilised in solution at 46·1° with this concentration of H-ion. This is rather significant and somewhat unique. With further increase in the H-ion concentration the solution loses its stability with gradual increase in the rate of its racemisation till at about $6·7 \times 10^{-4}$ molar it regains its normal uncatalysed value. But the increase in the specific inversion rate continues till at $1 \times 10^{-3}$ molar of H-ion there occurs a sharp break in the curve. Beyond $5 \times 10^{-2}$molar of H-ion the substance suffers decomposition by the acid. Even at 0·05 and 0·01 molar H-ion concentration $k$-values were unreliable for readings after half an hour. The values relating to these concentrations, given in the table, correspond to readings before any decomposition sets in.

Fig. 3

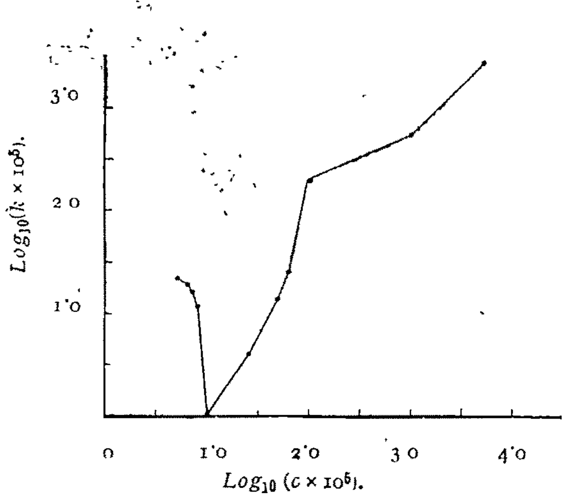
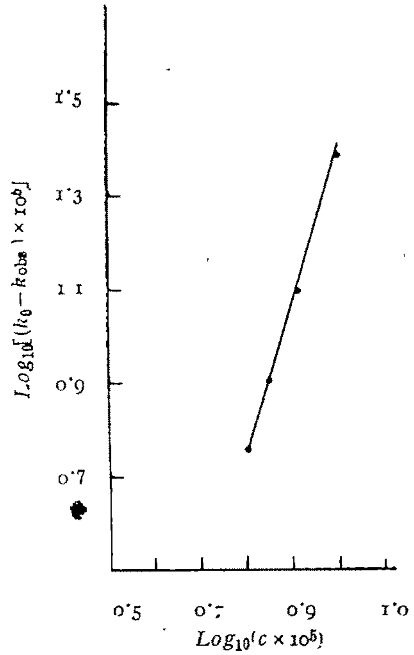


Fig. 4



If the difference between the normal uncatalysed velocity constant $k_0$, and the observed catalysed value $k_{obs}$, be plotted against concentration, a straight line is obtained for the concentration range where the catalytic effect is negative. This is shown in Fig. 4 with $\log_{10}(k_0 - k_{obs})$ plotted against $\log_{10}c$. Such straight line relationship cannot, however, be found for the remaining higher concentrations where the net effect is one of acceleration. Obviously, therefore, above the concentration of $1 \times 10^{-4}$ molar, two effects are superimposed—an additional accelerating influence besides the characteristic catalytic retardation. This acceleration is presumably associated with some partial and gradual change in the composition of the complex ion itself by the acid. This change may reasonably be attributed to the gradual formation of optically inactive *trans*-hydroxo-aquo-*bis*biguanide and diaquo-*bis*biguanide complexes. Evidences for the formation of the first type have already been referred to *(vide supra)*. The latter is likely to be formed at a comparatively increased concentration of HCl as all hydroxo-compounds tend to change into aquo-complexes in the presence of acids as shown below.

$$\left[Co(BigH^+)_3\right]Cl_3 \xrightarrow{H_2O} \left[\begin{matrix} HO \\ H_2O \end{matrix} Co(BigH^+)_2\right]Cl_2 \xrightarrow{HCl} \left[(H_2O)_2Co(BigH^+)_2\right]Cl_3.$$

It is more likely that both are formed and exist in equilibrium at all concentrations of the acid beyond $1 \times 10^{-4}$ molar (*cf.* the ascending portions of the curve, Fig. 3), the proportion of the diaquo-complex increasing with the acid concentration.

An analysis of the $k$-values, observed in the presence of various metallic ions (simple and complex) and recorded in Table VI may be made here.

The catalytic retardation due to univalent simple ions is considerably smaller than those of the polyvalent ones. Among themselves, $Tl^+$ is most effective and differs in this respect from the alkali metal and ammonium ions. This may be traced to the difference in the electronic structure

### TABLE VI

Catalyst—metallic ions

(1) Univalent

| Salt. | Conc. (mols./litre) | $k \times 10^6$. | Salt. | Conc (mols /litre). | $k \times 10^6$. |
|---|---|---|---|---|---|
| LiCl | $1 \times 10^{-1}$ | 10·40 | KCl | $0\ 5 \times 10^{-1}$ | 17·90 |
| $NH_4Cl$ | ,, | 11 80 | ,, | ,, | 18·0 (*d*) |
| NaCl | ,, | 18·30 | RbCl | $1 \times 10^{-1}$ | 9·63 |
| ,, | $0·5 \times 10^{-1}$ | 20·50 | CsCl | ,, | 8·55 |
| KCl | $1 \times 10^{-1}$ | 14·50 | TlCl | $1 \times 10^{-2}$ | 9·70 |

(2) Bivalent

| Salt. | Conc. (mols./litre) | $k \times 10^6$. | Salt. | Conc (mols /litre). | $k \times 10^6$. |
|---|---|---|---|---|---|
| $CaCl_2$ | $0·5 \times 10^{-1}$ | — | $BeCl_2$ | $0·1 \times 10^{-1}$ | 3·60 |
| ,, | $0·5 \times 10^{-2}$ | — | ,, | $0·5 \times 10^{-3}$ | 9·62 |
| ,, | $0·5 \times 10^{-3}$ | 9·70 | $MgCl_2$ | $0·1 \times 10^{-1}$ | 2·68 |
| $SrCl_2$ | $0·5 \times 10^{-1}$ | — | ,, | $0·5 \times 10^{-3}$ | 9.70 |
| ,, | $0·5 \times 10^{-2}$ | — | $ZnCl_2$ | $0·5 \times 10^{-3}$ | 5·44 |
| ,, | $0\ 5 \times 10^{-3}$ | 9·80 | $CdCl_2$ | ,, | 5 93 |
| $BaCl_2$ | $0·5 \times 10^{-1}$ | — | $HgCl_2$ | ,, | 3·34 |
| ,, | $0·5 \times 10^{-3}$ | 11·40 | $CuCl_2$ | ,, | 3·46 |
| ,, | ,, | 11·10 (*d*) | $MnCl_2$ | ,, | 3·46 |
| $PbCl_2$ | ,, | 15·20 | $CoCl_2$ | ,, | 10·80 |
| | | | $NiCl_2$ | ,, | 11·20 |

(3) Tervalent

| Salt. | Conc. (mols./litre) | $k \times 10^6$. |
|---|---|---|
| $AlCl_3$ | $0·1 \times 10^{-2}$ | 5·10 |
| ,, | $0·5 \times 10^{-3}$ | 6·06 |
| $LaCl_3$ | $0·1 \times 10^{-2}$ | 3·42 |
| ,, | $0\ 5 \times 10^{-3}$ | 3·95 |

(4) Quadrivalent

| Salt. | Conc. (mols./litre) | $k \times 10^6$. |
|---|---|---|
| $ZrCl_4$ | $0·5 \times 10^{-3}$ | 4·26 |
| $ThCl_4$ | $0·1 \times 10^{-2}$ | 4·18 |
| ,, | $0·5 \times 10^{-3}$ | 5 20 |

(5) Complex ions

| | | | | | |
|---|---|---|---|---|---|
| $[CO_3\,Co(NH_3)_4]Cl$ | $0·5 \times 10^{-3}$ | 7 55 | $[Co(NH_3)_6]Cl_3$ | $0·5 \times 10^{-3}$ | 8·69 |
| $[(NO_2)_2Co(NH_3)_4]Cl$ | ,, | 7·41 | $[Co(en)_3]Cl_3$ | ,, | 10·20 |
| $[Cu(BigH^+)_2]Cl_2$ | ,, | 3·56 | $[Cr(cn)_3]Cl_3$ | ,, | 9·07 |
| $[Ni(BigH^+)_2]Cl_2$ | ,, | 3 34 | $[Cr(BigH^+)_3]Cl_3$ | ,, | 10·10 |
| $[ClCo(NH_3)_5]Cl_2$ | ,, | 9·75 | $[Co(BigH^+)_3]Cl_3$ (racemic) | ,, | 24·60 (no effect) |

of $Tl^+$ ion which, unlike the alkali ions, does not possess an inert gas configuration. The catalytic activity of alkali ions excepting $Li^+$ follows the order of their ionic radius. Thus, $Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+$. $Li^+$ stands between $Rb^+$ and $NH_4^+$ in its catalytic power, instead of following $Na^+$ in order of its ionic volume. Lithium, therefore, differs from its congeners in this as in many other respects, presumably due to the helium like structure of its ion. $Tl^+$ with a radius of 1·49Å, which is almost equal to that of $Rb^+$, is much more powerful than even $Cs^+$.

The simple bivalent cations may be divided into four groups:—(*i*) those having inert gas structure—$Be^{++}$, $Mg^{++}$, $Ca^{++}$, $Sr^{++}$ and $Ba^{++}$; (*ii*) those with an outermost shell of 18 electrons—$Zn^{++}$, $Cd^{++}$ and $Hg^{++}$; (*iii*) ions with an outermost shell of 2 electrons—$Pb^{++}$; and (*iv*) ions of the first transitional series with variable electrons >8 and <18 in the outermost shell—$Mn^{++}$, $Co^{++}$, $Ni^{++}$ and $Cu^{++}$. The bivalent cations along with the ter- and quadrivalent ones possess very high retarding power. All the cations of group (*i*) are almost equally active. The values for $Be^{++}$ and $Mg^{++}$ suffer somewhat in their quantitative character due to hydrolysis. At a concentration of $0{\cdot}5 \times 10^{-2}$ molar $Ca^{++}$, $Sr^{++}$ and $Ba^{++}$ practically inhibit racemisation at the experimental temperature, no change of rotation being observed for the solution of the active salt for over 18 hours. Ions of group (*ii*) are somewhat stronger than those of group (*i*) in their catalytic power. Of these again $Hg^{++}$ appears to be the most active. This is rather striking in view of the fact that $HgCl_2$ is a very weak electrolyte. At the high dilution employed, however, it might suffer considerable dissociation into ions. Among the ions of the transitional series $Cu^{++}$ and $Mn^{++}$ are as powerful inhibitors as mercury. $Co^{++}$ and $Ni^{++}$, on the other hand, approach $Sr^{++}$ and $Ba^{++}$ in their catalytic effect. $Pb^{++}$, the only member of group (*iii*), is somewhat less active than $Ni^{++}$.

The ter- and quadrivalent ions that have been examined, with the exception of $Al^{3+}$, are slightly more active than $Zn^{++}$ and $Cd^{++}$. The effect of hydrolysis of the catalyst in all these cases obscures the results to a certain extent.

Among the complex ions that have been examined, those with octahedral configuration are comparatively less active than those with planar configuration. These latter, namely copper and nickel complexes, resemble the simple $Cu^{++}$, $Mn^{++}$ and $Hg^{++}$ ions in their power of catalytic retardation. The univalent octahedral complexes are again somewhat more effective than the bi- and tervalent ones. The latter approach the simple $Co^{++}$ ion in this respect.

A few measurements were made to study the catalytic racemisation also of the *d*-$[Co(BigH^+)_3]Cl_3$. The results are practically identical with those observed for its *l*-enantiomer. These are indicated by the letter *d* against the *k*-value in Table VI.

All the simple salts used as catalysts in these experiments were of guaranteed purity (Kahlbaum's *pro analysi*). The complex salts were all freshly prepared in a pure state in our laboratory.

### B. *Anions*

No appreciable catalytic activity due to anions was observed with the single exception of OH-ion, which, on the other hand, was found to accelerate enormously the rate of racemisation (Table VII).

The action of NaOH is rather irregular. Judging from the acceleration effect induced by $[Co(BigH^+)_3](OH)_3$, that due to NaOH in the first two cases is too small to fit in with the high OH-ion concentration of the solution. The retardation effect of the $Na^+$ is alone insufficient to account for this low value, as its catalytic activity at the concentration employed is of little significance. Some chemical interaction between NaOH and the reactant, besides the simple double decomposition, is likely to complicate the issue. To a certain extent this is indicated by a diminution of about 0·3 to 0·4 units in the $p_H$-value of the solution after a few hours or at the end of the experiment.

TABLE VII

| Substance. | Conc. (mols./litre). | $p_H$ (H-electrode). | Conc. of $OH^-$ (mols./litre) | $k \times 10^5$. |
|---|---|---|---|---|
| $[Co(BigH^+)_3](OH)_3$ | $0·5 \times 10^{-3}$ | 8·85 | $0·71 \times 10^{-5}$ | 542 |
| ,, | $0·375 \times 10^{-3}$ | 8·70 | $0·50 \times 10^{-5}$ | 496 |
| ,, | $0·25 \times 10^{-3}$ | 8·50 | $0·32 \times 10^{-5}$ | 448 |
| NaOH | — | 10·35 | $0·224 \times 10^{-3}$ | 32·5 |
| ,, | — | 10·95 | $0·89 \times 10^{-3}$ | 165 |
| ,, | — | 11·40 | $0·25 \times 10^{-2}$ | 1220 |

*Other anions*

TABLE VIII

Conc. (mols./litre) = $0·5 \times 10^{-3}$.

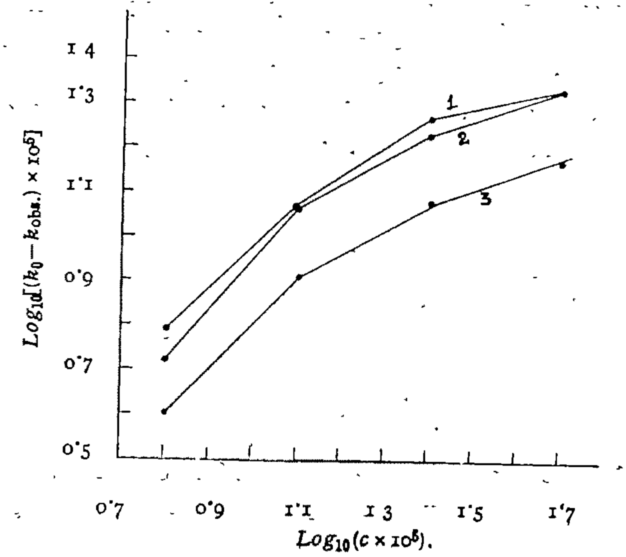
| Salt ... ... | KCl | KBr | KI | $KNO_3$. |
|---|---|---|---|---|
| $k \times 10^5$ ... ... | 23·3 | 22·8 | 22·8 | 22·8 |

The small retradation is due to $K^+$ only. Bivalent anions like $SO_4''$, $CO_3''$, etc., could not be used as they form precipitates with the complex ion.

### *The Concentration of the Catalyst and the Magnitude of Retardation*

It has already been shown that in the case of H-ion there is a direct linear relationship between the magnitude of retardation and the concentration of the catalyst within a certain range.

FIG. 5



A few experiments were, therefore, carried out to investigate if similar relationship also obtains in the case of other cations, specially the most potent ones, namely, $Ca^{++}$, $Mn^{++}$ and $Cu^{++}$. The results are summarised in Table IX and represented graphically in Fig. 5. All measurements were made at 46·1° with a 2% ($4·3 \times 10^{-2}$ molar) solution of $l$-$[Co(BigH^+)_3]Cl_3$. Two series of measurements were made at each concentration and the $k$-values given represent the mean of closely agreeing values of the two series.

Plotting the values of $\log_{10}c$ against those of $\log_{10}(k_0 - k_{obs.})$, no linear relationship could, however, be obtained.

Whether the catalyst acts by lowering the $PZ$-value, or increasing the activation energy of the molecule, or by affecting both, cannot be discussed for the present, unless a systematic investigation of the temperature coefficient of the catalysed racemisation for each catalyst is taken up.

TABLE IX

| Conc. (mols./litre) × $10^4$ | | ... | 5·0 | 2·50 | 1·25 | 0·625 | 0·3125 |
|---|---|---|---|---|---|---|---|
| $k \times 10^5$ | $CaCl_2$ | ... | 9·70 | 12·60 | 16·50 | 20·60 | 24·90 |
| ,, | $MnCl_2$ | ... | 3·46 | 7·79 | 13·10 | 19·40 | 24·40 |
| ,, | $CuCl_2$ | ... | 3·46 | 6·16 | 13·0 | 18·50 | 24·20 |

### *Mechanism of Racemisation*

Johnson and co-workers have, as already mentioned, shown that Thomas's theory of inversion, based on the assumption of secondary ionisation, cannot be supported, since the validity of his experimental evidences are open to serious question. The alternative view of an intramolecular rearrangement, due to Werner, has been advocated by them with an additional assumption of participation by the solvent. But before an interchange of two points of attachment in *cis*-positions necessary for such rearrangement can occur, there must be at least a momentary rupture of the chemical bonds at those positions, even though none of the chelate groups or molecules are completely detached from the central atom. This obviously involves the possibility of chemical decomposition during inversion even under conditions where the molecule is thermodynamically stable. Since all the six bonds in an octahedral complex are equivalent being of $d^2sp^3$ hybrid type, there is no reason why two such bonds attached to one and the same chelate group will not suffer similar rupture at the same time. There is, however, no experimental evidence of chemical decomposition being invariably associated with inversion. The suggestion, that such an interchange without any rupture of the chemical bond is possible if the bonds concerned move, along with the attached groups, towards each other, pass across and then interchange their position, is also untenable because of considerable steric hindrance involved in the mechanism.

A more probable hypothesis regarding the mechanism of racemisation may be based upon the following picture.

The free individual existence of the two enantiomers in the pure state, in spite of their having identical energy content, indicates that there is a potential barrier between them. Hence the supply of some activation energy is necessary for their interconversion. Addition of energy to a molecule leads to an increase in its translational, rotational and vibrational motions, and the molecule is said to be activated or excited. A molecule with a regular, octahedral configuration in its normal state, when excited with sufficient quanta of energy, may lose this configuration and assume another which is stable under the new conditions. On the subsequent removal of excess energy, the molecule returns again to its normal octahedral configuration, and since both *d*- and *l*-forms are endowed with equal energy content, there is equal probability for the formation of both. This results in a racemic product.

The nature of the configuration at the *excited* or *critically activated* state of the molecule may be represented by (*b*) in Fig. 1.

The configuration (*b*) may be viewed as derived from (*a*) when two pairs of octahedral bonds, holding the chelate groups *y* and *z* respectively, rotate in opposite directions along their own plane through an angle of 45°. The molecule under this condition may be regarded to assume a distorted or twisted octahedral (?) form, with bond angles between each pair remaining, however, unchanged at 90°. When the excited molecule afterwards returns to its normal state, it may either retrace its previous steps regenerating (*a*), or by a further rotation through 45° in the same direction as before, produce (*c*) which is identical with the mirror image of (*a*).

The molecule is not likely to lose its regular octahedral configuration until and unless the activation energy supplied is redistributed internally and transferred specifically to the rotational and vibrational degrees of freedom of the bonds concerned. This amounts to an increase in the time interval between *pre-activation* and *critical activation* with an increased chance of deactivation. The probabillty factor $P$ and hence the $PZ$-value will thereby be lowered, as we have found in the present case.

All evidences, therefore, indicate that inversion or racemisation of an optically active compound occurs through intramolecular rearrangements, as was first suggested by Werner, but not with the rupture of any chemical bond, even though momentary. Racemisation in the solid state also can be explained without difficulty on this basis.

Our best thanks are due to Prof. J. N. Mukherjee, for providing facilities of polarimetric measurements in his laboratory.

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# TRANSPORT NUMBERS OF AQUEOUS SILVER NITRATE IN PRESENCE OF SUCROSE AND MEASUREMENTS OF CONDUCTIVITY, VISCOSITY, DENSITY AND REFRACTIVITY

By Dushyant Narasingasa Solanki and Shankaranand Mukerji

Transport number measurements have been made at 25° for aqueous silver nitrate ($M/18$) in presence of varying proportions of sucrose. The minimum in the transport number-sucrose concentration curve has been attributed to the changes in the degree of hydration of sucrose Data are also given for the conductivity, viscosity, density and refractivity of the corresponding solutions.

The most extensive series of experiments on migration ratios is that of Hittorf (*Ann. Physik*, 1853, **89**, 177; 1859, **106**, 337, 513), the earliest worker in the field. Noyes (*Z. physikal. Chem.*, 1901, **36**, 63; *Technology Quarterly*, 1904, **17**, 4) made exact measurements of the migration ratios for a large number of salts. Steele (*Phil. Trans.*, 1902, **198A**, 105) concluded that the only possible cause of variability in the migration ratio with concentration was the formation of complex ions.* Diverging views prevail in the literature (*cf.* Carrara, *Gazzetta*, 1903, **33**, 241; Krumreich, *Z. Elektrochem.*, 1916, **22**, 446) regarding the influence of the medium on the transport number of silver nitrate despite considerable work done in this field.** It was of interest, therefore, to investigate the influence of sucrose on the transport number, especially from the standpoint of corresponding changes in conductivity, viscosity, density and refractivity of the medium.

## EXPERIMENTAL

The chemicals employed were Merck's guaranteed reagents. A stock solution of $M/9$-$AgNO_3$ was prepared. In all the following experiments this stock solution was used either after proper dilution or with the appropriate addition of sucrose. The transport number apparatus used was the one devised by Findlay (*Chem. News*, 1909, **100**, 185). It was first filled with $M/18$-$AgNO_3$ solution to the mark taking sufficient precaution to avoid the introduction of air bubbles. It was then rigidly fixed and kept in an air-thermostat maintained at $25 \pm 0{\cdot}1°$. It was afterwards connected with a source of E.M.F. and a current of 12-13 milliamps. sent through the solution for 2½ hours. The electrodes used were of pure silver. The current was obtained by tapping off a suitable potential from a 220 volt D. C. main. A milliammeter and a copper voltameter were also inserted in the circuit, in series. The coulometer solution was prepared according to Ottel's recommendations (*Chem. Ztg.*, 1893, **17**, 543). The copper plate to be used as cathode was first cleaned and weighed; and at the conclusion of the experiment it was withdrawn from the solution, washed well with distilled water and with alcohol, dried in the hot air over a flame, cooled and again weighed. While the experiment was in progress a slow stream of hydrogen, washed by bubbling through water, was passed through the coulometer solution in order to keep it stirred (*cf.* also Richards, Collins, and Heimrod, *Z. physikal. Chem.*, 1900, **32**, 321).

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* *cf.* also Noyes (*loc. cit.*); Bein (*Z. physikal. Chem.*, 1898, **27**, 1; 1899, **28**, 439); Cantelo and Payne (*J. Phys. Chem.*, 1932, **36**, 1045).

** *cf.* Schlundt (*J. Phys. Chem.*, 1902, **6**, 159); Carrara (*loc. cit.*); Jones and Basset (*Amer. Chem. J.*, 1904, **32**, 409); Jones and Rouiller (*ibid.*, 1906, **36**, 427); Sachanov and GrinBaum (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1769); Krumreich (*loc. cit.*).

At the conclusion of the experiment, the rubber tube connecting the anode and the middle compartments was closed by means of a clip, and the anode liquid run off, through the tap at the bottom of the anode tube, into a graduated cylinder. This tube and the electrode were then washed out with a little of *the original solution*, which was also collected in the cylinder and the volume noted. The composition of this, and of the original solution was determined volumetrically. Since the concentration changes on electrolysis in the vicinity of the electrodes are usually less, a slight error in the analysis will affect the transport number value to a considerable extent. Repeated analyses had therefore to be carried out to get the required accuracy. The solution from the middle compartment after electrolysis was also analysed from time to time and was found to remain almost unaltered in composition. From the increase, on electrolysis, of Ag-ion concentration in the anode compartment, the transport number of the cation was computed. The above quantity has been measured for $M/18$-$AgNO_3$ in presence of varying proportions of sucrose as shown in Table I.

TABLE I

*Influence of sucrose*

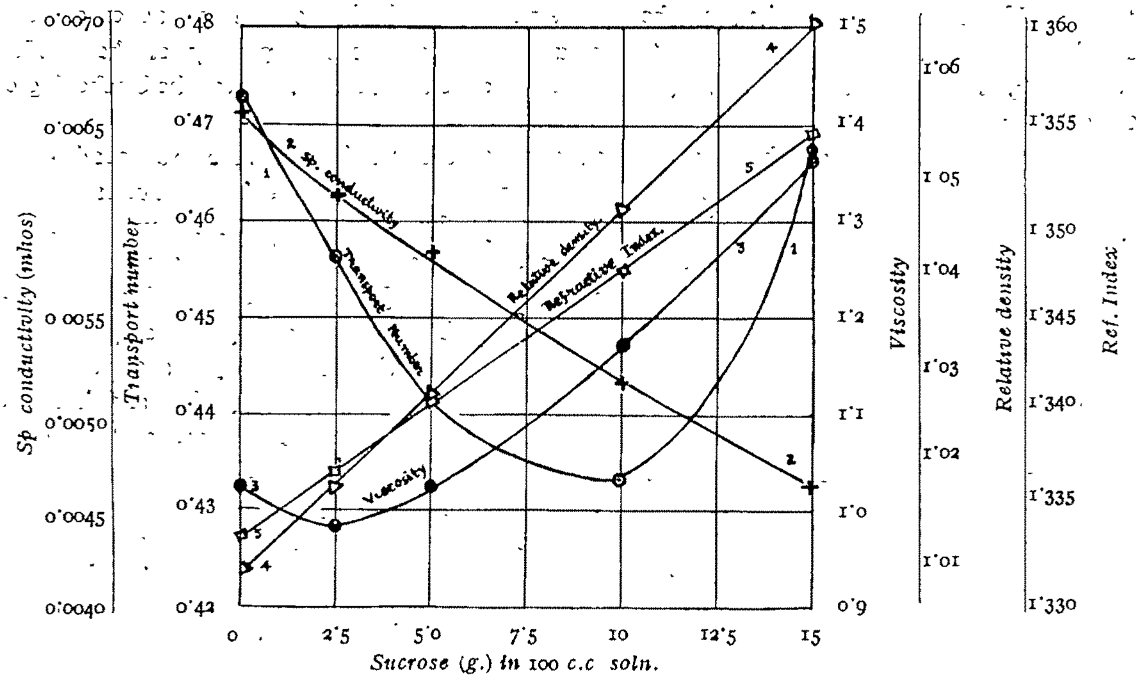
Conc. of $AgNO_3$ in the mixture $= M/18$. Temp. $= 25 \pm 0·1°$. Current $= 12$-$13$ milliamps.
Duration of electrolysis $= 2\frac{1}{2}$ hrs.

| Amounts of sucrose in 100 c.c. soln. | Transport No. of Ag.$^+$ | | Specific conductivity. | Viscosity ($\mu$.) centipoises. | Relative density. | Refractive index. ($n_D^{1}$) |
|---|---|---|---|---|---|---|
| 0 g. | 0·473<br>0·473<br>0·474 | 0·473 | 0·00655 mhos. | 1·020 | 1·008 | 1 33329 |
| 2·5 | 0·454<br>0·455<br>0·459 | 0·456 | 0 00614 | 0·981 | 1·017 | 1·33676 |
| 5·0 | 0·441<br>0·443<br>0·439 | 0·441 | 0·00584 | 1·025 | 1 027 | 1·34046 |
| 10·0 | 0·434<br>0·430<br>0·435 | 0·433 | 0·00516 | 1·173 | 1 046 | 1·34718 |
| 15·0 | 0·468<br>0·469<br>0·464 | 0·467 | 0·00462 | 1·363 | 1·065 | 1 35456 |

To obtain further information in regard to the above results the corresponding electrolytic conductivity was determined on a Pye's modified Post Office box with the usual precautions (*cf.* Joshi and Solanki, *J. Indian Chem. Soc.*, 1937, **14**, 323; 1940, **17**, 627). The cell constant, determined by using $N/50$-KCl, was found to be 0·3777. These results are given in column 3, Table I.

The viscosity and relative density determinations were also made at 25° for each of the above mixtures and are shown in Table I. The refractive indices for the sodium line corresponding to these were determined by means of Pulfrich refrac tometer at the above temperature and these results are given in Table I.

All these results are shown graphically in Fig. 1. The quantities, *viz.*, transport number, specific conductivity, viscosity, relative density, and refractive index, are plotted against concentration of sucrose in the mixture by appropxim ate selection of scale units in the same figure (*cf.* curves 1-5 in Fig. 1).



## DISCUSSION

The transport number of an ion depends, besides the factors like temperature, valency, concentration and the nature of the solute and the other ion with which it is associated, upon the specific behaviour, the dielectric constant and the viscosity of the medium. The abnormalities in the above quantity especially in stronger solutions are usually attributed to the formation of molecular or ionic complexes in the conducting medium, owing to the interaction of the ions with the solute or the solvent molecules.

Results in column 2, Table I indicate that the transport number of $Ag^+$-ion diminishes progressively with the increase in concentration of sucrose till it attains the minimum value in the vicinity of 10%, and then suddenly rises (*cf.* curve 1, Fig. 1). To account for the observed results, the following disturbing factors need be considered: (*i*) hydration of the cation, $[Ag(H_2O)_n]^+$; (*ii*) complex formation of $Ag^+$-ion with sucrose molecules, $[Ag(sucrose)_n]^+$, (*iii*) hydration of sucrose $[sucrose\ n(H_2O)]$.

(*i*) and (*ii*) might bring about the migration of water and sucrose molecules respectively along with $Ag^+$-ion, with a concomitant change in the concentration of sucrose. Polarimetric observations of the solutions *after* migration, however, indicated no measureable changes in the sucrose concentration in the anode and cathode compartments. Washburn (*J. Amer. Chem. Soc.*, 1909, **31**, 322), however, observed a change in concentration of the reference substance (sucrose or rafinose) after electrolysis; this was maximum in the case of LiCl and minimum in KCl. It appears, therefore, that (*i*) and (*ii*) are not operative. Furthermore, $Ag^+$-ion being relatively a heavier ion might show very little tendency for hydration, since ions of lighter elements are more highly hydrated. The observed changes in the transport number value might be due principally to an increase in hydration of sucrose with its increased concentration, followed by a diminution in solvation. Among other physical factors influencing the mobility of an ion, reference should particularly be made to the dielectric constant of the medium and the specific frictional coefficient of the ions especially at higher concentrations of sucrose. Furthermore, sucrose at a high concentration might disturb the homogeneity of the $AgNO_3$ solution by forming the colloidal silver particles by reduction, as evident from the blackening of the solution.

When transference numbers in different solvents are considered there are found many inexplicable anomalies. Attempt at arriving at any generalisation has been found impossible owing to the fact that the above measurements by different authors have produced divergent data. To quote a few: Schlundt (*loc. cit.*) determined the transport number of $Ag^+$-ion from $AgNO_3$ in water and in various organic liquids; Jones and Basset (*loc. cit.*) and Jones and Rouiller (*loc. cit.*) measured the transport number in water, methyl and ethyl alcohols, acetone and in binary mixtures of these solvents together with the conductivity of such solutions; Sachanov and GrinBaum (*loc. cit.*) conducted measurements in aniline, pyridine and in mixed solutions of the two; Carrara (*loc. cit.*) in methyl alcohol; and Krumreich (*loc. cit.*) in ethyl alcohol-water mixtures. Their results and interpretations differ very widely.

Kruger (*Z. Elektrochem.*, 1916, **22**, 445) on theoretical grounds, concluded that the transport numbers of a given pair of ions should tend to the same value in all non-associated solvents. In associated solvents, and when solvation occurs, the values differ. He remarks that in dilute solutions, the above values for $AgNO_3$ are practically independent of the nature of the solvent (*cf.* also Sachanov, *J. Phys. Chem*, 1917, **21**, 169). Kruger believes that the effect of the solvent may be covered, in a simple case, by its viscosity: $u\eta = c_1$ and $v\eta = c_2$, where $u$ and $v$ are the mobilities and $c_1$, $c_2$ are constants.

It became necessary for the interpretation of the results obtained to determine the specific conductivity, viscosity, density and refractivity of the solutions used in this work. These data are shown in Table I and graphically in curves 2-5 in Fig. 1. The linear relationship of specific conductivity, density and of refractivity with concentration of sucrose, as revealed by the respective straight line graphs (*cf.* curves 2, 4 and 5 in Fig. 1) suggests that these measurements seem to throw practically no light in accounting for the minimum in the transport number curve. The viscosity graph exhibits a minimum in the neighbourhood of 3% (*cf.* curve 3 in Fig. 1), which it is difficult to account for. It is interesting, however, to note that the variations of viscosity and transport number are of the same nature, though the actual positions of the minima are not the same. It is seen that the effect of changing viscosity on the addition of sucrose is important in affecting the conductance and the ionic mobilities, but no general conclusions can, apparently, be drawn (*cf.* also Partington, Taylor's "Treatise on Physical Chemistry," MacMillan and Co. Ltd., London, 1931, Vol. I, p. 729).

Our best thanks are due to Dr. S. S. Joshi, Head of the Department of Chemistry, for valuable help and suggestions during the course of this work.

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# SYNTHESIS OF *dl*-PINONIC ACID

By P. L. Narasimha Rao

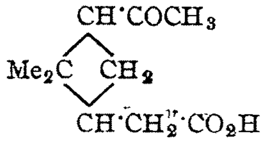
The direct total synthesis of *dl*-pinonic acid is effected. This amounts to a new total synthesis of pinocamphone and also of the α-and β-pinenes.

Pinonic acid, the well known oxidation product of α-pinene, has been of more than usual interest. The presence of tetramethylene ring in α-pinene itself was inferred from its constitution. Starting from this acid, Ruzicka and Trebler (*Helv. Chim. Acta*, 1924, **7**, 489) effected a partial synthesis of pinocamphone and thus α-and δ-pinenes. The acid itself exhibits mutarotation in its active forms and is very labile (Delèpine, *Bull Soc. Chim.*, 1036, *v*, **3**, 1369). Tiemann (*Ber.*, 1896, **29**, 3015) claimed to have effected an unusual synthesis of this acid from dihydrodihydroxy-α-campholenic acid involving a contraction of a *cyclo*pentane ring to a *cyclo*butane ring which was, however, recently disproved by Komppa and Beckmann (*Ber.*, 1936, **69B**, 2783). Attempts at synthesis of pinonic acid (I) were also made (*i*) by Komppa and Klami (*Ber.*, 1937, **70**, 788) and Guha, Ganapathi and Subramanian (*Ber.*, 1937, **70**, 1505) by means of Arndt and Eistart's reaction (*Ber.*, 1935, **68**, 200) using diazomethane on *cis*-pinonoyl chloride and (*ii*) by Guha, Ganapathi and Subramanian (*loc. cit.*) by Blaise's reaction on the acid chloride of 2:2-dimethyl-1-carboxy-*cyclo*butane-3-acetonitrile. Attempts were also made by the latter authors to synthesise it from pinic acid. Guha and Narasimha Rao (*Ber.*, 1938, **71**, 1591; *J. Indian Inst. Sci.*, 1940, **22A**, 317) reported a series of attempts to synthesise it from pinic acid.

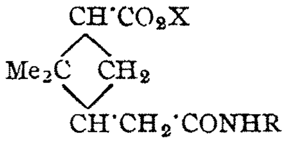
Pinonic acid being an oxidation product of α-pinene and pinocamphone (Wallach and Engel brecht, *Annalen*, 1906, **346**, 236) may be taken as synthesised from the elements now that these natural products have been synthesised (Guha and Narasimha Rao, *J. Indian Inst. Sci.*, 1940, **22A**, 226; Komppa, Klami and Kuvaja, *Chem. Abst.*, 1941, 5878). But this would be more a degradation of the natural products than a real scientific synthesis of pinonic acid from the elements.

The direct total synthesis of pinonic acid has now been accomplished starting from *trans*-pinic acid, synthesised by Guha, Ganapathi, and Subramanian (*loc. cit.*).

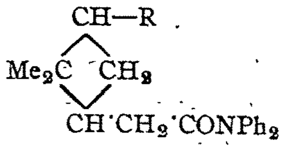
Attempts have been made in the past to prepare a suitable derivative of pinic acid such as (II) with a view to applying Blaise-Mair's reaction for the synthesis of a pinonic acid derivative (Guha and Narasimha Rao, *loc. cit.*). This could not be successfully carried out because of the difficulty of effecting a preferential hydrolysis of the ester grouping in compounds of the type (II) (R=.NHPh, $-NH.C_6H_4NO_2$, and $-NH_2X$, X=Et).



(I)



(II)



(III)

It has now been found that this difficulty could be overcome by hydrolysing the diphenyl derivative (III, $R=CO_2Et$), m.p. 99-100°, by means of 95% sulphuric acid and, the acid (III, $R=CO_2H$), m.p. 139-40°, was obtained in very good yields although the preferential hydrolysis of the ester group in (III, $R=CO_2Et$) could also be effected, but less readily, by means of castor seed lipase and 10% alcoholic potash. A Grignard's reaction on the acid chloride of (III, R = $CO_2H$) as is to be expected, went beyond the stage of the formation of the ketone (III, R = COMe) but Blaise-Maire's reaction using zinc methyl iodide produced only traces of a ketone (separated and tested by Girard's reagent) giving mainly the methyl ester of (III, R = $CO_2H$). This behaviour of the acid chloride of (III, R = $CO_2H$) towards zinc methyl iodide appears to be very similar to that of benzoyl chloride as observed by Gilman and Gelson (*Rec. trav. chim.*, 1936, **55**, 518). In view of these circumstances, a reaction was tried using acid chloride of (III, R = $CO_2H$) and cadmium dimethyl (or cadmium methyl halide), and (III, R = COMe) was then obtained in about 30% yield. It was characterised by semicarbazone, m.p. 204-205°, identical with a sample prepared from alkali-treated pinonic acid. It gave on hydrolysis pinonic acid (semicarbazone, m.p. 204-5°). The synthetic pinonic acid has been characterised also by its ethyl ester and ethyl ester semicarbazone. All these derivatives are identical with those prepared from an authentic specimen of pinonic acid. On oxidation in the usual manner, *dl*-pinonic acid gave *dl*-pinoylformic acid.

This synthesis of *dl*-pinonic acid amounts to a new total synthesis of pinocamphone and of the pinenes.

## EXPERIMENTAL

trans-1-*Carbethoxy*-2:2-*dimethyl*cyclo*butane*-3-*acetdiphenylamide* (III, R = $CO_2Et$) was prepared from *trans*-1-carbethoxy-2:2-dimethyl*cyclo*butane-3-acetyl chloride (Guha and Narasimha Rao, *Ber.*, 1938, **71**, 1594) (12 g.), diphenylamine (18·5 g.) and pyridine (30 c.c.). The gummy reaction product was washed free of pyridine with water and dried over sulphuric acid for a week. It was then crystallised from benzene and then several times from alcohol. It separated from alcohol in colourless stout prisms, m.p. 99-100°. (Found: C, 75·5; H, 7·5; N, 3·8. $C_{23}H_{27}O_3N$ requires C, 75·6; H, 7·4; N, 3·8 per cent).

trans-2:2-*Dimethyl*cyclo*butane*-3-*acetdiphenylamide*-1-*carboxylic acid* (III, R = $CO_2H$) was prepared by saponification of the ester (III, R = $CO_2Et$). The hydrolysis with alkali reagents, castor seed lipass and benzene sulphonic acid were unsatisfaotory as mixtures of compounds were formed too difficult to separate and the yields of acid (III, R = $CO_2H$) were loo low to be of any practical value. The following method gave almost quantitative yield of the acid. The ester (10 g.) and sulphuric acid (95%, 80 c.c.) were heated together at 60-65° for 2½ hours when a homogeneous solution resulted. The product was poured on to crushed ice and the gummy product (which hardened after a while) was separated, washed and purified by dissolving in cold alkali and precipitation with dilute sulphuric acid. The acid was finally crystallised once from benzene and twice from alcohol from which it separated in lustrous prismatic plates or stout prisms, m.p. 139-40°. (Found: C, 74·7; H, 6·8; N, 4·2; Equiv., 337. $C_{21}H_{23}O_3N$ requires C, 74·8; H, 6·8; N, 4·2 per cent. Equiv., 337). The acid on hydrolysis with 15% alcoholic potash for 24 hours gave pinic acid identified as its amide and esterification by alcohol-sulphuric acid method gave back the ester (III, R = $CO_2Et$).

*Action of Methyl Magnesium Iodide on the Acid Chloride of* (III, R = $CO_2H$).—A Grignard's ragent (1/50 mol.), prepared from magnesium and methyl iodide in the usual manner, was allowed to react with an ethereal solution of acid chloride of (III, R = $CO_2H$) (prepared from 7·1 g. of the acid and thionyl chloride) at 0°. The gummy reaction product, isolated in the usual manner, gave back a small quantity of the acid (III, R = $CO_2H$) but the major portion was neutral. It gave no semicarbazone and when treated with Girard's pyridine reagent, no ketone could be detected. On hydrolysis with 10% methyl alcoholic potash, diphenylamine and 2:2-dimethyl-

*cyclo*butane-1-dimethylcarbinol-3-acetic acid identified as its ester (Guha and Narasimha Rao, *loc. cit.*) were isolated.

*Action of Zinc Methyl Iodide.*—A Blaise-Maire's reaction using zinc methyl iodide (from 12 g. of zinc-copper couple and 3 c.c. of methyl iodide) was conducted at 0° in the usual way with the acid chloride of (III, $R=CO_2H$) (prepared from 14·2 g. of the acid by the thionyl chloride method) dissolved in benzene. As there was no evidence of any reaction, the solution was warmed up to room temperature and kept for a day. Working up in the usual manner, 6 g. of the unchanged acid were recovered while the neutral fraction (A) which partly solidified, was tested for ketones by Girard's pyridine reagent. The aqueous solution of ketonic-Girard reagent complex gave a precipitate with Mayer's alkaloidal reagent and evaporation of the ethereal extract after the removal of non-ketonic bodies gave only a minute amount of a gummy residue. A portion of the neutral fraction (A) was saponified by aqueous alkali and only methyl alcohol and acid (III, $R=CO_2H$) could be detected in the reaction products.

Attempts to increase the yield of the ketonic fraction by conducting the Blaise-Maire's reaction at the boiling point of benzene were unsuccessful.

trans-dl-*Pinonic acid Diphenylamide* (III, R=COMe) *by the action of Cadmium Methyl Halide on the Acid Chloride of* (III, R=COOH).—The Grignard solution (150 c.c.) containing methyl magnesium bromide, prepared from 1 g. of magnesium, was decomposed by finely powdered anhydrous cadmium chloride (7·1 g.) in a manner similar to that described by Gilman and Nelson (*loc. cit.*). An ethereal solution (100 c.c.) containing the acid chloride of (III, R=COOH) (prepared from 10 g. of the acid) was added dropwise with shaking and the reaction was then completed by boiling on the water-bath for 2½ hours. After leaving overnight, it was decomposed with cracked ice and dilute sulphuric acid (10%, 300 c.c.) and thrice extracted with ether. From the ether solution unchanged acid (6·1 g.) was recovered by extracting with 10% sodium bicarbonate solution. After drying over sodium sulphate the ethereal solution was evaporated and the transparent gummy residue was used for further work as it could not be obtained crystalline in contact with the usual solvents. The yield of the product estimated by its semicarbazone is about 30% after allowing for the recovered acid. The semicarbazone of the ketone (III, R=COMe) crystallised from alcohol in slender prismatic plates, m.p. 204-5°. (Found: N, 14·0. $C_{23}H_{28}O_2N_4$ requires N, 14·3 per cent). The melting point of the semicarbazone was undepressed when admixed with a genuine sample prepared from pinonic acid (*vide infra*).

dl-*Pinonic Acid.*—The diphenylamide (6·1 g.) and methyl alcoholic potash (10%, 50 c.c.) were boiled under reflux for 24 hours on a steam-bath. After distillation of methyl alcohol, the product was diluted with water (30 c.c.) and extracted with ether to remove diphenylamine. The aqueous solution was acidified with ice-cold 50% sulphuric acid, saturated with ammonium sulphate and repeatedly extracted with small portions of chloroform. After washing with a saturated solution of ammonium sulphate and drying over anhydrous sodium sulphate, the chloroform extract was evaporated *in vacuo*. The residue (3 g.), a pale yellow transparent gum, did not solidify when kept in ice-chest under vacuum for over a fortnight.* (Found: Equiv., 185. $C_{10}H_{16}O_3$ requires Equiv., 184). The semicarbazone, prepared in the usual manner and crystallised from alcohol, melted at 205° which remained undepressed when admixed with a genuine sample of *dl*-pinonic acid semicarbazone. (Pinonic acid was prepared for purposes of comparison by treating *cis-dl*-pinonic acid with strong alkali and reprecipitation by acid as described below). The ethyl ester, prepared by alcohol-sulphuric acid method, boiled at 145-6°/15 mm. The ester semicarbazone was found to be identical with a genuine sample of ethyl *dl*-pinonate semicarbazone by mixed melting point method.

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* After the paper has been communicated for publication it has been found that *dl*-pinonic acid crystallised slowly after about 2 months. After 3 recrystallisations from water it melted at 103-5° (colourless leaflets) undepressed when admixed with a genuine sample of Baeyer's α-pinonic acid, m.p. 104-5°. The aqueous mother-liquors gave an oily pinonic acid.

*Preparation of* dl-*Pinonic Acid Diphenylamide from* cis-*Pinonic Acid for purposes of comparison with the synthetic sample*.—*cis-dl*-Pinonic acid (m.p 106-7°) (obtained by oxidation of *dl*-α-pinene according to the method of Slawinski and Zacharewicz, *Rocznick. Chem.*, 1934, **14**, 213) was purified by once crystallisation from benzene, twice from hot water and twice from methyl alcohol. The acid (5 g.), dissolved in excess of 4*N*- sodium hydroxide, was warmed on the water-bath for 12 hours in order to hasten the isomerisation and establishment of the equilibrium between the *cis* and *trans*-isomers (*cf.* Delépine, *loc. cit.*). After keeping at the room temperature for a day, the chilled alkaline solution was acidified with 6*N*- sulphuric acid, extracted 4 times with chloroform and the extract dried over sodium sulphate. After removal of the solvent *in vacuo* a gummy residue was obtained which crystallised rather slowly. The acid mixture (5 g.) was treated with thionyl chloride (4 g.) in dry chloroform (15 c.c.) and warmed on the water-bath for 15 minutes. After removal of chloroform and thionyl chloride, the acid chloride, dissolved in benzene (25 c.c.), was poured into a solution of diphenylamine (4·4 g.) in pyridine (20 c.c.). The reaction product after keeping for 1 hour on the water-bath was poured into excess of 2*N*- dilute sulphuric acid and extracted with chloroform. The extract after drying over anhydrous sodium sulphate was evaporated. The residue, a clear yellow gum, did not solidify in contact with the usual solvents. It was analysed after drying for a week *in vacuo* over sulphuric acid. (Found: N, 4·2. $C_{22}H_{25}O_2N$ requires N, 4·2 per cent). The *semicarbazone*, m.p. 205-6°, crystallised in colourless glistening plates. (Found: N, 14·1. $C_{23}H_{28}O_2N_4$ requires N, 14·3 per cent).

My sincere thanks are due to Prof. P. C. Guha for his keen interest in the progress of these investigations. My hearty thanks are also due to Mr. T. George Verghese for the help rendered in connection with some of the analyses recorded in this paper.

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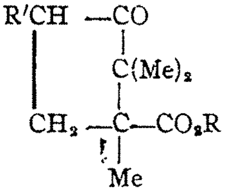
# ON AN UNAMBIGUOUS SYNTHESIS OF CAMPHOR. PART I. SYNTHESIS OF CAMPHONONIC ACID

By N. C. Ganguly

Trimethyl camphoronate, synthesised by a new method in excellent yield, is converted into trimethyl homocamphoronate by Arndt and Eistart's reaction and camphononic acid is obtained by Dieckmann condensation of homocamphoronic ester and subsequent hydrolysis.

Homocamphoric acid was ketonised to camphor by several methods and this acid was synthesised by Haller and Blanc (*Compt. rend.*, 1899, **130**, 376) from campholide, a lactone obtained by the reduction of camphoric anhydride. As any of the carbonyl groups of the anhydride may be affected in the process, the structure of the resulting campholide, from the synthetic point of view, remains ambiguous. This work has been undertaken to effect a synthesis of homocamphoric acid in a way, which will leave little doubt as regards its constitution. It has been proposed to use camphononic acid (I, R=R′=H) as the starting material and to add the acetic acid residue with the help of Reformatsky's reaction. This paper describes the synthesis of camphononic acid.

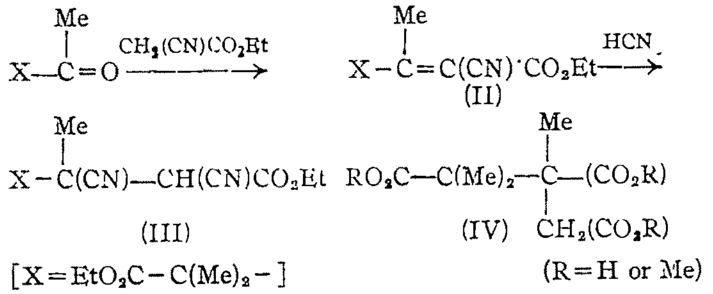


(R=H, Me or Et; R′=H or $CO_2Me$)

(I)

Camphononic acid is an important degradation product of camphor and was isolated by Walker and Henderson (*J. Chem. Soc.*, 1896, **69**, 755) in a very small quantity as a by-product during the electrolysis of $\beta$-methyl hydrogencamphorate. It was later on prepared by Lapworth and Chapman (*J. Chem. Soc.*, 1899, **75**, 985) from dibromocamphor, which when oxidised with nitric acid in the presence of silver nitrate yielded a tribasic acid, the anhydride of which on pyrolysis gave camphononic acid. Lapworth (*J. Chem. Soc.*, 1900, **77**, 1070) also obtained this acid by the permanganate oxidation of dehydrohomocamphoric acid. These methods of production throw some light on its constitution but confirmatory evidence for its structure has been supplied by Lapworth and Lenton (*J. Chem. Soc.*, 1901, **79**, 1286), who had been able to degrade camphanamide to camphononic acid by two distinct methods, the reactions being easily explicable on the assumption of structure (I, R=R′=H) for camphononic acid. The final confirmation of the constitution by synthesis, which had been so long lacking, has now been supplied. We have used camphoronic acid as the starting material. Camphoronic acid is also a cleavage product of camphor and was obtained by Kachler (*Ber.*, 1880, **13**, 487) and Balbiano (*Ber.*, 1897, **30**, 1901) along with isomeric acidic residues during oxidative degradations of camphor. Bredt assumed this $C_9H_{16}O_6$ acid to be $\alpha\alpha\beta$-trimethyltricarballylic acid and this was confirmed by its synthesis by Perkin and Thorpe (*J. Chem. Soc.*, 1897, **71**, 1169). Unfortunately the yield in this synthesis is extremely poor and the method cannot be employed for any practical purpose. We have been, however, successful in substituting it with an alternate satisfactory method for its synthesis. The above method embodies the general scheme for the synthesis of tricarballylic acids by Hope and Sheldon (*J. Chem. Soc.*, 1922, **121**, 2227).

Ethyl dimethylacetoacetate is condensed with ethyl cyanoacetate in glacial acetic acid solution under the catalytic influence of acetamide (Cope, *J. Amer. Chem. Soc.*, 1937, **59**, 2327) when the resulting ethyl α-cyano-βγγ-trimethylglutaconate (II) is isolated in good yield. The unsaturated ester adds to itself a molecule of hydrogen cyanide and ethyl αβ-dicyano-βγγ-trimethylglutarate (III) is obtained in good yield; saponification of this dicyano ester is accomplished by refluxing with 72% sulphuric acid for thirty hours. Camphoronic acid (IV, R=H), isolated in the usual manner, is found to be contaminated with some of its anhydride. The crude product on treatment with aqueous alkali and careful acidification furnishes the acid, which after one crystallisation from water melts at 168°. This is converted by diazomethane into the triester (IV, R=Me) in quantitative yield. The whole of the operation can be completed in a very short time and 100 g. of dimethyl acetoacetic ester furnish 20 g. of pure camphoronic acid.



$$X{-}\overset{Me}{\overset{|}{C}}{=}O \xrightarrow{CH_2(CN)CO_2Et} X{-}\overset{Me}{\overset{|}{C}}{=}C(CN){\cdot}CO_2Et \xrightarrow{HCN}$$

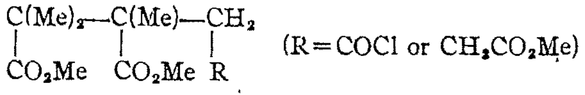
(II)

$$X{-}\overset{Me}{\overset{|}{C}}(CN){-}CH(CN)CO_2Et \qquad RO_2C{-}C(Me)_2{-}\overset{Me}{\overset{|}{\underset{\underset{CH_2(CO_2R)}{|}}{C}}}{-}(CO_2R)$$

(III) (IV)

$[X=EtO_2C-C(Me)_2-]$ (R=H or Me)

Camphoronic ester has then been converted into homocamphoronic ester in a very good yield by means of Arndt and Eistart's reaction, utilising the technique recently developed by Bachmann *et al* (*J Amer. Chem. Soc.*, 1940, **62**, 834) in his ingeneous synthesis of equilenin. Mono acid chloride (V, R=COCl) of the primary carboxylic group of trimethyl camphoronate is prepared by partial hydrolysis of the triester with alcoholic alkali and subsequent treatment with thionyl chloride in the presence of pyridine and the acid chloride is then converted into the corresponding diazoketone by means of diazomethane. The diazoketone (not isolated), on treatment with methanol in presence of freshly prepared silver oxide, yields trimethyl homocamphoronate (V, $R=CH_2CO_2Me$). Homocamphoronic ester when treated with sodium dust in presence of a few drops of alcohol furnishes the keto-ester (I, R=Me and $R'=CO_2Me$) in good yield. A trace of sodium ethoxide has been found to be essential for initiating the reaction. The ester on hydrolysis with an excess of 20% sulphuric acid yields camphononic acid, which crystallises out of the reaction mixture on cooling. The acid after crystallisation from dilute hydrochloric acid melts at 230-31°. Noyes (*Amer. J. Chem.*, 1901, **28**, 483) recorded the melting point of *dl*-camphononic acid to be 232°. The ester and oxime of the keto-acid have also been described.



$$\underset{CO_2Me}{\underset{|}{C(Me)_2}}{-}\underset{CO_2Me}{\underset{|}{C(Me)}}{-}\underset{R}{\underset{|}{CH_2}} \qquad (R=COCl \text{ or } CH_2CO_2Me)$$

(V)

## EXPERIMENTAL

*Ethyl α-Cyano-βγγ-trimethylglutaconate* (II).—A mixture of ethyl dimethylacetoacetate (100 g.), ethyl cyanoacetate (57 g.), acetamide (16 g.) and glacial acetic acid (120 c.c.) was slowly distilled at about 115° from a fractionating Claisen's flask. In course of 8 hours 110 c.c. of acetic acid were collected. The residue, after dilution with water, was extracted with ether and the ethereal layer washed thrice with large excess of water and dried. After removal of ether, the product was fractionated. Almost the whole of the unreacted dimethylacetoacetic ester and cyanoacetic ester came over as a constant boiling mixture at a low temperature and the condensation product (21 g.) was collected at 140-145°/4 mm. On redistillation it boiled at 145°/4 mm. (Found: N, 5·48. $C_{13}H_{19}O_4N$ requires N, 5·53 per cent).

*Ethyl αβ-Dicyano-βγγ-trimethylglutarate* (III).—Potassium cyanide (13 g.), dissolved in water (70 c.c.), was slowly added with shaking to a solution of ethyl α-cyano-βγγ-trimethylglutaconate (21 g.) in alcohol (120 c.c.). The mixture was cooled in ice and a cold solution of hydrochloric acid (16 c.c., *d*, 1·15) in water (11 c.c.) was slowly added. It was left as such at the room temperature (28°) for about 25 minutes and then acidified with hydrochloric acid (16 c.c.) in water (250 c.c.). A heavy oil separated out. The oil was taken up in ether and the ethereal solution washed with water and dried over sodium sulphate. After removal of ether ethyl αβ-dicyano-βγγ-trimethylglutarate was collected at 170°/5 mm. (Found: N, 9·76. $C_{14}H_{20}O_4N_2$ requires N, 10·0 per cent).

*Camphoronic acid* (IV, R=H).—The above dicyano ester (5 g.) was mixed with 20 c.c. of concentrated sulphuric acid and left overnight. It was next diluted with 15 c.c. of water and refluxed on a sand-bath for 30 hours. The resulting clear solution was diluted with water and after saturation with ammonium sulphate extracted several times with ether. The ethereal solution was washed with a small amount of water and dried over sodium sulphate. The solid acid, obtained after removal of ether, was warmed with dilute potassium hydroxide solution on a water-bath. On careful acidification of the cooled solution and repeated extraction with ether 4 g. of the crude camphoronic acid, melting at 156-160°, were obtained. This was then twice crystallised from water when beautiful prisms, melting at 168°, were obtained. (Found: C, 49·36; H, 6·34. $C_9H_{14}O_6$ requires C, 49·54, H, 6·42 per cent).

Trimethyl camphoronate was obtained by esterifying camphoronic acid with an ethereal solution of diazomethane. The ester was isolated as colourless mobile liquid boiling at 134°/3 mm. (Found: C, 54·93; H, 7·64. $C_{12}H_{20}O_6$ requires C, 55·36; H, 7·69 per cent).

*Trimethyl Homocamphoronate* (V, $R=CH_2{\cdot}CO_2Me$).—Partial hydrolysis of trimethyl camphoronate was effected by refluxing trimethyl camphoronate (2·6 g.) for 2 hours with a mixture of methanol (50 c.c.) and *N*-sodium hydroxide solution (10 c.c.). Methanol was removed under reduced pressure at 40° and the residue, after dilution with water, was acidified with very dilute hydrochloric acid. The separated oil was taken up in ether and dried over sodium sulphate. The ether was driven off at the ordinary temperature under vacuum. The oily diester acid was next dissolved in dry benzene (8 c.c.) and 4 drops of pyridine added and the resulting solution was cooled in ice-water. Freshly distilled thionyl chloride (3 c.c.) was added to it and the mixture was allowed to stand for ½ hour at the ordinary temperature and finally warmed for 10 minutes at 40°. The solution was then evaporated under reduced pressure and freed of last traces of thionyl chloride. A cold solution of the acid chloride in benzene (32 c.c.) was added with shaking to an ice-cold solution of diazomethane in ether. The diazomethane was prepared in *n*-propyl alcohol and absolutely pure ether was used. A solution of nitrosomethylurethane in pure ether was decomposed by dropping on a solution of potassium hydroxide in *n*-propyl alcohol and the evolved gas was dissolved in the usual way in ice-cold ether. The diazomethane solution, thus prepared, was cooled in ice and the acid chloride was slowly added to it. The ether and the excess of diazomethane were driven off under reduced pressure at room temperature. The diazo-ketone (gummy), thus obtained, was decomposed with freshly prepared silver oxide in methanol solution following strictly the procedure of Bachmann *et al* (*loc. cit.*). The solution, after decomposition, was kept as such overnight. It was next boiled with animal charcoal and filtered and finally distilled. Trimethyl homocamphoronate (2 g.) distilled at 150-155°/5 mm. On redistillation the triester boiled at 150°/5 mm. (Found: C, 56·57; H, 7·9. $C_{13}H_{22}O_6$ requires C, 56·93; H, 8·02 per cent).

dl-*Camphononic Acid*.—Trimethyl homocamphoronate (12 g.), sodium dust (2 g.), dry benzene (50 c.c.) and a few drops of alcohol were heated on a water-bath for 12 hours, when all metallic sodium disappeared. The cooled mixture was poured into cold dilute acetic acid. After extraction with ether, the ethereal layer was washed successively with water, sodium bicarbonate solution and water again and then dried over calcium chloride. On distillation 7·5 g of the β-ketonic ester (I, R=Me; R′=$CO_2Me$) were obtained, b.p. 157°/9 10 mm. (Found: C, 59·8; H, 7·5. $C_{12}H_{18}O_5$ requires C, 59·5, H, 7·4 per cent). The bicarbonate wash of the above ethereal extract was acidified and re-extracted with ether. On removal of ether about 1 g. of a gummy product was obtained which together with the above β-ketonic ester (7 g.) were refluxed with 100 c.c. of 20% sulphuric acid for 20 hours Solid crystals separated on cooling, which after filtration and crystallisation from dilute hydrochloric acid with the aid of charcoal melted at 230-31°. (Found: C, 63·9; H, 8·6; Equiv., 171. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2; per cent Equiv., 170).

Oxime of above keto-acid was prepared by refluxing an alcoholic solution of the keto-acid with hydroxylamine hydrochloride and pyridine. On crystallisation from water it melted at 189-90°. Literature records m.p. 186-87° (Lapworth and Lenton, *J. Chem. Soc.*, 1901, **79**, 1292). (Found: N, 7·6. $C_9H_{15}O_3N$ requires N, 7·6 per cent).

Ethyl ester of the keto-acid was prepared by refluxing 5·4 g of the acid with alcohol (55 c.c.) and sulphuric acid (*d*, 1·84, 3 c.c.) for 36 hours. On working up in the usual manner the ester (4·5 g.) boiled at 106-110°/8 mm. (Found: C, 66·5; H, 8·8. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1 per cent).

The author is indebted to Prof. P. C. Mitter and Dr. S. K. Mitter for their advice and interest during this investigation and to Mr. N. N. Ghosh, for carrying out the microanalyses.

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# INFLUENCE OF NON-ELECTROLYTES ON THE DECOMPOSITION POTENTIAL OF AQUEOUS SILVER NITRATE

By Dushyant Narasingasa Solanki

Decomposition potential of aqueous silver nitrate ($N/10$) has been measured at 30°, in presence of the non-electrolytes: ethyl alcohol, glycerine, acetone and pyridine, whose concentrations have been varied within wide limits. Results show that the above quantity for silver nitrate practically remains unaltered despite the presence of large proportions of the non-electrolytes (except acetone) in the system. These together with the results with acetone are discussed. The data are also given for the conductivities of the corresponding solutions.

Le Blanc (*Z. physikal. Chem.*, 1891, **8**, 299; 1893, **12**, 333; 'A Text Book of Electrochemistry' MacMillan Co., London, 1920, Chap. VIII, p. 289) was the first to measure the decomposition voltages of acids, bases and salts in aqueous solutions. The work was further extended by subsequent investigators to a large number of salts, both in aqueous* and non-aqueous† solutions. The limitations of the graphical method have been pointed out by many workers**. The influence of the electrode material on the decomposition potential was studied by Coehn and Dannenberg (*Z. physikal. Chem.*, 1901, **38**, 609) and Caspari (*ibid.*, 1899, **30**, 89), and of irradiation of the electrodes by Leighton (*J. Phys. Chem.*, 1913, **17**, 695).

The experiments were carried out with a view to examining the influence of medium on the decomposition potential of silver nitrate in presence of some non-electrolytes.

## EXPERIMENTAL

The chemicals employed were Merck's reagents. Ethyl alcohol, acetone and pyridine were freshly distilled before use. Pure glycerol was used. A stock solution of $N/5$-$AgNO_3$ was prepared. In all the following experiments 50 c.c. of the stock solution diluted to 100 c.c. with the requisite amount of nonelectrolyte and water, were used for electrolysis. The electrolysis was carried out in a conductivity cell between two bright platinum electrodes, each of 1 sq. cm. area, fixed vertically, the inter-electrode distance being 1·2 cm. The cell was kept immersed in a water thermostat maintained at 30±0·1°. The platinum electrodes before use were properly cleaned; they were placed in $N/10$-$AgNO_3$ solution and short-circuited for several hours (*cf.* Findlay, "Practical Physical Chemistry", Longmans, Green & Co., London, 1933, p. 205) until they no longer gave any detectable E.M.F. when placed in the same solution. A storage battery (6 volts) was closed through a suitable resistance furnished with a sliding contact. A gradually increasing potential was applied to the poles of the cell containing the solution under investigation and the current passing was read on a precision milliammeter. The potential applied was measured by the potentiometer, supplied by the Cambridge Instrument Co., Ltd. It was worked on a steady

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* *cf* Smale *Z. physkal. Chem.*, 1894, **14**, 577; Glaser, *Z. Elektrochem.*, 1898, **4**, 373, 424; Kudra, *Mem. Inst. Chem. Ukrain Acad. Sci.*, 1938, **5**, 127, 177; *cf.* also Heyrovsky and co-workers, Die Polarographische Methode in Bottger, "*Physikalische Methoden der chemischen Analyse*," Leipzig.

† *cf* Muller and Duschek, *Monatsh*, 1922, **43**, 75; Mason and Mathews, *J. Phys. Chem.*, 1925, **29**, 1379: Finkelstein, *Z. physikal. Chem.*, 1925, **116**, 303; Biswas and Bose, *ibid.*, 1927, **125**, 442; Evans, Lee and Lee, *J. Amer. Chem. Soc.*, 1935, **57**, 489.

** *cf.* Emil Bose, *Z. Elektrochem.*, 1898, **5**, 153; Westhaver, *Z. physikal. Chem.*, 1905, **51**, 65; Bennewitz, *ibid.*, 1910, **72**, 202; *cf.* also Ferguson and van Zyl, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 337.

2 volt battery and was adjusted before use by using Weston's standard cadmium cell and was checked after the completion of an experiment. Each experiment was repeated at least twice using fresh solution and cleaned electrodes. The current-voltage values are shown in Table I and also graphically in Fig. 1.

TABLE I*

*Current-voltage values for*
$N/10$-$AgNO_3$.
Temp. = 30°.

| Applied potential in volts. | Current in milliamps. | Applied potential in volts. | Current in milliamps. |
|---|---|---|---|
| 0 613 | 0 | 0·931 | 1·0 |
| 0·649 | 0 | 0·992 | 2·0 |
| 0·720 | 0 | 1·034 | 3·1 |
| 0·738 | 0 | 1·099 | 4·5 |
| 0·783 | 0·08 | 1·137 | 5·6 |
| 0·828 | 0·15 | 1·208 | 7·5 |
| 0·845 | 0·22 | 1·250 | 8·7 |
| 0·869 | 0·37 | 1·307 | 10·4 |
| 0·888 | 0·50 | 1·428 | 13·7 |

TABLE II

*Influence of ethyl alcohol.*
Conc. of $AgNO_3 = N/10$
Temp. = 30°.

| Vol. of EtOH in 100 c.c soln. | Decomposition voltage | Rssistance. (ohms.) | Sp. condy (mhos.) |
|---|---|---|---|
| 0 c.c | 0·75 | 33·5 | 0·01127 |
| 5 | 0·75 | 35 | 0·01079 |
| 10 | 0·75 | 37 | 0·01021 |
| 25 | 0·75 | 52 | 0·00726 |
| 50 | 0·75 | 77·5 | 0·00487 |

TABLE III

*Influence of glycerol.*
Conc. of $AgNO_3 = N/10$.
Temp. = 30°.

| Vol of glycerol. in 200 c.c. soln. | Decomposition voltage (graphical). | Resistance. (ohm.) | Sp condy. (mhos.) |
|---|---|---|---|
| 0 c.c. | 0·75 | 33·5 | 0·01127 |
| 5 | 0·75 | 35 | 0·01079 |
| 10 | 0·75 | 40 | 0·00944 |
| 25 | 0·75 | 55 | 0·00687 |
| 50 | 0·75 | 121 | 0·00312 |

* Table I serves as a specimen table, where the current-voltage values are given In Tables II-V only the final results obtained from graphs (*cf.* curves 2-5 in Fig 1) are shown.

TABLE IV

*Influence of acetone.*

Other conditions same as in Table III.

| Vol. of acetone in 100 c.c. soln. | Decomposition voltage (graphical). | Resistance. | Sp. condy |
|---|---|---|---|
| 0 c.c. | 0·75 | 33·5 ohm. | 0·01127 mho. |
| 5 | 0·85 | 34 | 0·01111 |
| 10 | 0·85 | 36 | 0·01049 |
| 50 | 0·85 | 56 | 0·00674 |

TABLE V

*Influence of pyridine.*

Other conditions same as in Table III.

| Vol of pyridine in 100 c.c. soln. | Decomposition voltage (graphical.) | Resistance. | Sp. condy. |
|---|---|---|---|
| 0 c.c. | 0·75 | 33·5 ohm. | 0·01127 mho. |
| 5 | 0·75 | 51 | 0·00740 |
| 10 | 0·75 | 55 | 0·00687 |
| 25 | 0·75 | 67 | 0·00564 |

The electrolytic resistances of the solutions used in this work were determined on a Post Office box with the usual precautions. These values are shown in Tables II-V.

## DISCUSSION

The foregoing results in Table I indicate the variation of the current as shown by the milliammeter when a gradually increasing potential is applied to the electrodes. At first, an almost zero or very small current, the residual current, is obtained, but after the applied E.M.F. reaches a certain value, the current begins to increase rapidly with increase in the applied E.M.F. The point, where this rapid increase in the electrolysing current commences, is the *decomposition potential* of the solution under consideration. A sudden and marked change in the direction of the curve obtained by plotting the applied E.M.F. against the current strength (*cf.* Fig. 1) indicates the decomposition point. This is in agreement with the general findings of the earlier workers, Le Blanc (*loc. cit.*), Glaser (*loc. cit.*), Emil Bose (*loc. cit.*), Bennewitz (*loc. cit.*) and others. When a dilute solution of silver nitrate is electrolysed between platinum electrodes, silver is deposited on the cathode and oxygen is liberated at the anode. A cell of the type, Ag | solution | $O_2$, is set up, which exhibits a certain E.M.F. due to the tendency of the silver and oxygen to pass back into the ionic state. The E.M.F. of the cell acts in a direction opposite to that of the electrolysing current. In order, therefore, that continuous electrolysis may take place, an E.M.F. must be applied to the electrodes sufficient to overcome the back E.M.F. of the products of electrolysis. This explains why a certain minimum potential is necessary to induce continuous decomposition in an electrolyte (*cf.* also Le Blanc, *loc. cit.*).

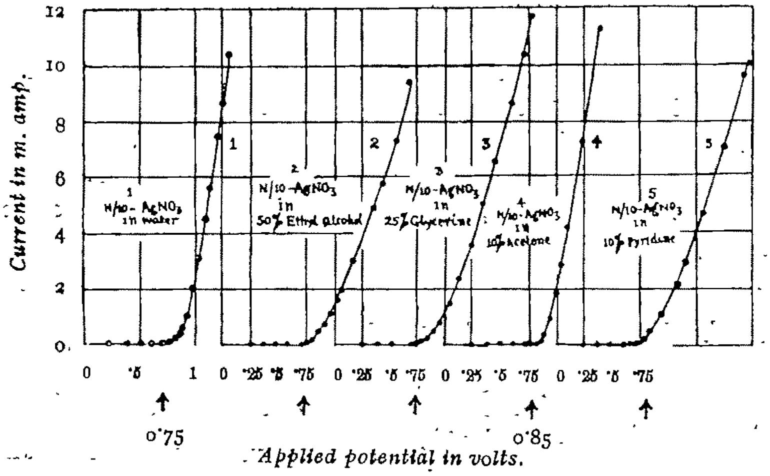
The value recorded in the present paper for the decomposition potential, obtained by the graphical method is 0·75 volt for $N/10$-$AgNO_3$ at 30°; Le Blanc (*loc. cit.*) gives 0·70 volt for $N$-$AgNO_3$ presumably at 20°. The observed increase from 0·7 to 0·75 volt might be mainly due to a decrease in concentration of $AgNO_3$ solution from $N$ to $N/10$, since temperature coefficient of the decomposition potential is negligibly low, 0.0008 volt per degree (*cf.* Wilkinson and Gillet, *loc. cit.*). It is well known that a smaller E.M.F. is required to separate an ion from a concentrated solution than from a dilute one (*cf.* Le Blanc, *loc. cit.* Bose, *loc. cit.* and Wilkinson and Gillet, *loc. cit.*).

Results with ethyl alcohol (Table II) and glycerine (Table III) show that the decomposition potential of $N/10$-$AgNO_3$ remains almost unaltered, despite the addition of varying amounts (5 to 50%) of the nonelectrolyte (curves 2, 3 in Fg. 1). It is interesting to note that the changes (though of a considerable magnitude in some cases) in physical properties of the medium such as the viscosity, density, conductivity, and dielectric constant. seem to have no effect on the decomposition potential of $AgNO_3$. This might probably be attributed to the absence of interaction between the ions of the solute and the medium. Similar were the conclusions of Biswas and Bose (*loc. cit.*), who observed that the presence of water in methyl alcohol solutions of KI and KBr had very little influence on the corresponding current-voltage curves. But the presence of water in methyl alcohol solutions of HCl and LiCl had a marked influence on the decomposition potentials; this was attributed by the authors to the combination of the solute with the solvent. Contrary views are held regarding the influence of the medium on the transport number of the silver ion in silver nitrate. Carrara (*Gazzetta*, 1903, **33**, 241) assumed that no complex ion was found in the medium, while others notably Krumreich (*Z. Elektrochem.*, 1916, **22**, 446) found it necessary to assume the formation of an alcohol-water complex (and not the solute-solvent complex) to account for the maximum in the transport number curve. Carrara's conclusions were further criticised by Lapworth and Partington (*J. Chem. Soc.*, 1911, **99**, 1417). Jones and Basset (*Amer. Chem. J.*, 1904, **32**, 409) and Jones and Rouiller (*ibid.*, 1906, **36**, 427) determined the relative migration velocities of the ions of silver nitrate in water, methyl and ethyl alcohol, acetone and in binary mixtures of these solvents together with the conductivity of such solutions. The relative migration velocities are influenced largely by the nature of the solvent and in mixed solvents are found to vary both with temperature and composition of the mixture probably due to the varying degrees of combination of the solvent with one of these ions.

The results in Tables II and III have already been explained on the assumption that the ions of the solute, *viz.*, $AgNO_3$, form no complex with the medium. It is, however, very likely that the added non-electrolyte (ethyl alcohol, glycerol) might form complexes with water, the exact composition of the complex depending upon the nature of the non-electrolyte and the relative proportions of the two. Sufficient evidence is available in the literature to show this possibility. Krumreich (*loc. cit.*) from transport number measurements of $AgNO_3$ in ethyl alcohol-water mixtures brought out evidence for the existence of alcohol-water complex Complex of the type, $C_2H_5OH \cdot 3H_2O$, corresponding to 50% alcohol, has been shown to exist beyond doubt by Dorochewski and Roshestwenski (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 860) from conductivity measurements and by Hess (*Ann. Physik*, 1908, **27**, 609) from volume contraction measurements. This is also in agreement with the views of Getman, Dunstan and Traube ("Viscosity," Monogram on Inorganic and Physical Chemistry Series, 1914). Glycerine is also known to form complexes with water. It should, however, be stressed at this stage that the existence of such water-alcohol or water-glycerine complexes in the medinm may not, it is to be anticipated, alter the decomposition potential of a dissolved solute ($AgNO_3$), provided the solute itself takes no part in complex formation with the medium, or its heat of solution is not affected appreciably. This follows from the fact that the decomposition potential of a solute is a thermodynamical quantity and should, therefore, correspond to the energy equal to the heat of formation of the solute from its ions.

Results with increasing proportion of pyridine (up to 25%) also indicate that the decomposition potential of silver nitrate remains unaltered, *i.e.*, 0·75 volt (Table V and Fig. 1). The above explanation might suitably account for the observed results provided $AgNO_3$ forms no complex with pyridine. Schlundt (*J. Phys. Chem.*, 1902, **6**, 159) from transport number measurements of $Ag^+$-ion from $AgNO_3$ in anhydrous pyridine, observed that $AgNO_3$ forms a complex with pyridine (*cf.* also Neustadt and Abegg, *Z. physikal. Chem.*, 1909, **69**, 486). Furthermore, Muller and Duschek (*loc. cit.*) determined the decomposition potentials of $AgNO_3$ in anhydrous pyridine. The values reported are 2·15 and 2·05 volts for $N/10$-$AgNO_3$ and $N$-$AgNO_3$ respectively. The abnormally high value 2·15 volts for $N/10$-$AgNO_3$ in pyridine obtained by Muller and Duschek (*loc. cit.*) as compared with the present value 0·75 volt in water (Table I) and in various mixtures

Fig. 1



of water and pyridine (Table V) might possibly be ascribed to the existence of silver nitrate-pyridine complexes in the former. Since the decomposition potential is not altered (*cf.* Fig. 1) though the proportion of pyridine in water-pyridine mixtures is varied up to 25%, it appears that silver nitrate-pyridine complex may not exist under the stated conditions, probably due to the decomposing action of water which is in a relatively larger proportion (*cf.* Henderson, *Z. physikal. Chem.*, 1907, **59**, 118; 1908, **63**. 325).

From the data returned in Table IV (curve 4 in Fig. 1) it is seen that the presence of acetone, (5%) raises the decomposition potential from 0·75 to 0·85 volt. Its increased concentration (up to 50%), however, produces no further change in the above quantity. This might probably be due to the formation of a stable complex of silver nitrate with acetone present in the various acetone-water mixtures used. It is also probable that the heat of the solution of silver nitrate might be affected considerably by acetone present in the system; this, however, might not happen in the case of ethyl alcohol, glycerol and pyridine.

It became necessary for the interpretation of the results obtained to determine the conductivities of the solutions used in this work. These data are shown in Tables II-V. Schall (*Z. physikal. Chem.*, 1894, **14**, 701) found that the conductivity is usually decreased when water is replaced in part by alcohol in solution, which is in agreement with the foregoing results. Hantzsch (*Z. anorg. Chem.*, 1900, **25**, 332) studied the influence of non-electrolyte on the conductivity of electrolytes. The addition of methyl alcohol, ethyl alcohol and acetone to aqueous solutions of the alkali and alkaline-earth metals diminished the conductivity slightly and approximately to the same extent.

In conclusion the author expresses his indebtedness to Prof. S. S. Joshi, for suggesting the problem and giving valuable help and criticism during the course of the present investigation.

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# CHARGE AND STABILITY OF COLLOIDS. PART II. EFFECT OF NON-ELECTROLYTES

By B. P. Yadava

The effects of non-electrolytes such as methyl alcohol, ethyl alcohol, agar agar, and gelatine have been studied from the view-point of the variation in the adsorption of oppositely charged ions by the colloidal particles of arsenious sulphide and ferric hydroxide sols. It has been observed that the sol is sensitised in the case of methyl alcohol whereas stabilised in the case of other non electrolytes.

Sensitisation of hydrophobic sols by non-electrolytes and specially hydrophilic colloids in low concentrations, is a very general phenomenon. It has also been observed that some non-electrolytes impart stability and specially some of these hydrophilic sols in larger concentrations produce considerable protection.

Various theories have been advanced from time to time to explain the phenomenon of sensitisation and protection. Freundlich and Löning ("Kaiser Wilhelm Gesellschafts-Festschrift," 1921, p. 82) consider that sensitisation is due to the presence of colloidal ions in the lyophilic sols. They suggest that the non-electrolyte is adsorbed on the surface of the colloidal particles. Pauli and Kitaj (*Kolloid Z.*, 1938, **82**, 43) explain sensitisation by supposing that an exchange takes place between the oppositely charged groups of the hydrophobic and the hydrophilic colloids.

Both the phenomena, *i.e.* the adsorption suggested by Freundlich and the exchange supposed to take place at the surface of the colloidal particles by Pauli, should lead to the lowering of the charge (*cf.* Weiser, *J. Phys. Chem.*, 1924, **28**, 1253) and due to this a sensitisation may occur. This is further confirmed by Freundlich assuming that sensitisation takes place when the hydrophobic sol is in excess and the hydrophilic sol must contain colloidal ions with charges opposite to those of the hydrophobic sols. On the other hand, Freundlich says "that protection is due to the adsorption of the hydrophilic sol on the particles of the hydrophobic sol so as to surround the latter and form a layer round it." It follows from this that the protective action certainly does not depend upon a strong charge being communicated to the particle.

It appears from the above, therefore, that when protection takes place the charge on the colloidal particle should not necessarily increase appreciably.

In this paper adsorption of oppositely charged ions by the colloidal particles of arsenious sulphide sol and ferric hydroxide sol has been measured by the method given in Part I of this series of papers (*J. Indian Chem. Soc.*, 1943, **20**, 25) in presence of various non-electrolytes and hydrophilic colloids in varying concentrations in order to find out how the adsorption varies under different conditions. Under limitations as pointed out in the previous paper of this series (*loc. cit.*) charge on the colloidal particles has been calculated from the amount of "chemical adsorption" alone, on the assumption that at the coagulating concentration of the electrolytes the adsorbed ions displace all ions of the same sign in the double layer.

## EXPERIMENTAL

The experimental procedure followed in this paper is the same as the one given in Part I (*loc. cit.*). With arsenious sulphide sol and methyl alcohol a sensitisation has been observed. The coagulating concentrations for a particular sol of known concentration, when methyl alcohol in a given percentage is added to the sol, are given in Table I.

TABLE I

Sol conc. = 16·16 g./litre. Sol taken = 5 c.c. Total volume = 10 c.c.

| | | | | | |
|---|---|---|---|---|---|
| Methyl alcohol added (% by volume) | ... | 0 | 1 | 10 | 25 |
| Coagulating conc. of $N/80$-$BaCl_2$ added (c.c.) | ... | 1·500 | 1·375 | 1·250 | 1·200 |

In measuring the adsorption with methyl alcohol the results obtained at coagulating concentrations are given in Table II(A). Here we observe that the adsorption decreases. Adsorptions were also measured when the concentration of the electrolyte was greater than the coagulating concentration and the results obtained are given in Table II(B). In this case also it is seen that the adsorption of the oppositely charged ion decreases. In all other cases the coagulating concentrations of the electrolytes have been added both in presence as well as in absence of the non-electrolyte in question. In the above table the percentage by volume has been calculated on the amount of the volume of methyl alcohol to 100 c.c. of the pure sol and not in total volume of the mixture.

The results obtained with arsenious sulphide and ferric hydroxide sols in presence of methyl alcohol, ethyl alcohol, agar agar, and gelatine are given in the following tables.

TABLE II

*Variation in the adsorption of* Ba-*ions by the particles of* $As_2S_3$ *sol when* MeOH *added in increasing conc. to it*

**A.** Sol conc. = 16·16 g./litre. Radius of the particle = 75$\mu\mu$ (by extrapolation). Sol taken = 100 c.c. Total vol. = 200 c.c. No. of particles in the sol = $2{\cdot}574 \times 10^{14}$.

| Nature of sol. | $N/80$-$BaCl_2$ added. | Adsorption of Ba-ions. Total | Physical. | Chemical. | Charge (e.s u. × $10^5$). |
|---|---|---|---|---|---|
| Sol+water | 30 c c. | 0·00365 g. | 0·00041g. | 0·00324 g. | 5·31 |
| Sol+1·0 c.c. MeOH+$H_2O$ | 27·5 | 0·00291 | 0·00043 | 0 00248 | 4·06 |
| Sol+10 c.c. MeOH+$H_2O$ | 25·0 | 0·00273 | 0·00045 | 0·00228 | 3·76 |
| Sol+25 c.c. MeOH+$H_2O$ | 24·0 | 0·00260 | 0·00045 | 0·00215 | 3·49 |

**B.** Sol conc. = 24·18 g./litre. Radius of the particle = 75$\mu\mu$ (by extrapolation). Sol taken = 250 c.c. Total vol. = 500 c.c. No. of particles in the sol = $9{\cdot}627 \times 10^{14}$. The electrolyte added is above coagulating conc.

| Nature of sol. | $N/20$-$BaCl_2$ added. | Adsorption of Ba-ions. Total. | Physical. | Chemical | Charge (e s u. × $10^5$). |
|---|---|---|---|---|---|
| Sol+water | 25·0 c.c. | 0·0135 g. | 0·0016.g. | 0·0119 g. | 5·21 |
| Sol+2·5 c.c. MeOH + $H_2O$ | 26·0 | 0·0109 | 0·0017 | 0·0092 | 4·03 |
| Sol + 5 c.c. MeOH+$H_2O$ | 26·5 | 0·0102 | 0·0017 | 0·0085 | 3·72 |
| Sol + 10 c.c. MeOH + $H_2O$ | 26·5 | 0·0099 | 0·0018 | 0·0081 | 3·56 |
| Sol+20 c.c. MeOH + $H_2O$ | 26·5 | 0·0096 | 0·0019 | 0 0077 | 3·37 |

From Table II it is clear that the adsorption of oppositely charged ions by the colloidal particles definitely decreases whether we add just the coagulating concentration or above it.

TABLE III

*Variation in the adsorption of* Ba-*ions by the colloidal particles of* $As_2S_3$ *sol with increasing concentrations of* EtOH *and* 0·2% *agar agar*

**A.** Sol conc. = 24·0 g./litre. Radius of the particles = 75$\mu\mu$ (by extrapolation). Sol taken = 250 c.c. Total vol. = 500 c.c. No. of particles in the sol = 9·557 × $10^{14}$.

| Nature of sol. | N/20-$BaCl_2$ added. | Adsorption of Ba-ions. Total. | Physical | Chemical | Charge (e.s.u. × $10^5$). |
|---|---|---|---|---|---|
| Sol + water | 25·0 c.c. | 0·0135g. | 0·0016g. | 0·0119g. | 5·25 |
| Sol + 2·5 c.c. EtOH + $H_2O$ | 26·0 | 0·0153 | 0·0018 | 0·0135 | 5·96 |
| Sol + 5 c.c. EtOH + $H_2O$ | 26·5 | 0·0143 | 0·0019 | 0·0124 | 5·47 |
| Sol + 10 c.c. EtOH + $H_2O$ | 26·5 | 0·0141 | 0·0019 | 0·0122 | 5·38 |
| Sol + 20 c.c EtOH + $H_2O$ | 26·5 | 0·0140 | 0·0020 | 0·0120 | 5·29 |

**B.** Sol conc. = 23·75 g./litre. Radius of the particles = 75$\mu\mu$ (by extrapolation). Sol taken = 250 c.c. Total vol. = 500 c.c. No. of particles in the sol = 9·46 × $10^{14}$.

| Nature of sol. | N/20-$BaCl_2$ added. | Adsorption of Ba-ions. Total. | Physical. | Chemical. | Charge (e.s.u. × $10^5$) |
|---|---|---|---|---|---|
| Sol + water | 25·0 c.c. | 0·0135g. | 0·0016g. | 0·0119g. | 5·29 |
| Sol + 2·5 c.c. agar + $H_2O$ | 26·0 | 0·0145 | 0·0018 | 0·0127 | 5·66 |
| Sol + 5 c c. agar + $H_2O$ | 26·5 | 0·0140 | 0·0018 | 0·0122 | 5·44 |
| Sol + 10 c.c. agar + $H_2O$ | 26·5 | 0·0137 | 0·0019 | 0·0118 | 5·26 |
| Sol + 20 c.c agar + $H_2O$ | 26·5 | 0·0134 | 0·0019 | 0·0115 | 5·12 |

TABLE IV

Sol conc. = 22·76 g./litre. Radius of the particles = 75 $\mu\mu$ (by extrapolation). Sol taken = 250 c.c. Total vol. = 500 c.c. No. of the particles in the sol = 9·063 × $10^{14}$. Conc. of the gelatine used = 0·32% by weight.

**A.** *With increasing concentration of unwashed gold label gelatine.*

| Nature of sol. | N/20-$BaCl_2$ added. | Adsorption of Ba-ions. Total. | Physical | Chemical. | Charge (e.s.u. × $10^5$). |
|---|---|---|---|---|---|
| Sol + water | 25·0 c.c. | 0·0134g. | 0·0016g. | 0·0118g. | 5·49 |
| Sol + 2·5 c.c. gelat. + $H_2O$ | 26·0 | 0·0137 | 0·0017 | 0·0120 | 5·59 |
| Sol + 5·0 c.c. gelat. + $H_2O$ | 26·5 | 0·0136 | 0·0018 | 0·0118 | 5·49 |
| Sol + 10 c.c. gelat. + $H_2O$ | 26·5 | 0·0133 | 0·0019 | 0·0114 | 5·30 |
| Sol + 20 c.c. gelat. + $H_2O$ | 26·5 | 0·0130 | 0·0019 | 0·0111 | 5·16 |

**B.** *With increasing concentration of washed iso-electric gelatine.*

| Nature of sol. | N/20-$BaCl_2$ added. | Adsorption of Ba-ions. Total. | Physical. | Chemical. | Charge in (e.s.u. × $10^5$), |
|---|---|---|---|---|---|
| Sol + water | 25·0 c.c | 0·0134g. | 0·0016g. | 0·0118g. | 5·49 |
| Sol + 2·5 c.c. gelat + $H_2O$ | 26·0 | 0·0136 | 0·0017 | 0·0119 | 5·54 |
| Sol + 5·0 c.c. gelat. + $H_2O$ | 26·5 | 0·0134 | 0·0017 | 0·0117 | 5·44 |
| Sol + 10 c.c. gealt. + $H_2O$ | 26·5 | 0·0128 | 0·0018 | 0·0110 | 5·14 |
| Sol + 20 c.c. gelat. + $H_2O$ | 26·5 | 0·0127 | 0·0019 | 0·0108 | 5·02 |

The concentrations of the sol as well as of the gelatine used in Table IV(B) are exactly the same as those used in Table IV(A).

The following are the results obtained with a positively charged ferric hydroxide sol which was dialysed for about a month. Its purity and concentration are: conc. = 9·104 g./litre: chlorine content of the sol = 0·5484 g./litre; radius of the particles = 50$\mu\mu$ (by extrapolation).

TABLE V.

*Variation of Adsorption of $SO_4$-ions by colloidal $Fe(OH)_3$.*

Number of the particles as calculated in the sol. [illegible]

A. *With increasing conc. of* MeOH

B. *With increasing conc. of freshly distilled* EtOH.

Adsorption of $SO_4$-ions.

Adsorption of $SO_4$-ions.

| Nature of sol | N/50 $K_2SO_4$ added | Total | Physical | Chemical | Charge (e.s.u. × $10^5$) | N/50 $K_2SO_4$ added | Total | Physical | Chemical | Charge (e.s.u. × $10^5$) |
|---|---|---|---|---|---|---|---|---|---|---|
| Sol+water | 20.0 c.c. | 0.0438 g. | 0.00351 g | 0.0403 g. | 5.17 | 20.0 c.c. | 0.0438 g | 0.00351 g | 0.0403 g | 5.17 |
| Sol+1 c.c. ROH+$H_2O$ | 21.0 | 0.0417 | 0.00353 | 0.0382 | [illegible] | [illegible] | 0.0490 | [illegible] | [illegible] | 5.84 |
| Sol+10 c.c. ROH+$H_2O$ | 22.5 | 0.0405 | 0.00356 | 0.0369 | 4.73 | 22.5 | 0.0483 | 0.00354 | 0.0448 | 5.76 |
| Sol+20 c.c. ROH+$H_2O$ | 22.5 | 0.0384 | 0.00358 | 0.0348 | 4.47 | 22.5 | 0.0477 | 0.00356 | 0.0441 | 5.68 |
| Sol+40 c.c. ROH+$H_2O$ | 22.5 | 0.0360 | 0.00359 | 0.0324 | 4.16 | 22.5 | 0.0473 | 0.00358 | 0.0437 | 5.62 |

R in **A** stands for Me and in **B** for Et

TABLE VI.

Sol taken = 10 c.c. [illegible] = 4.694 × [illegible]

A. *With increasing conc. of 0.25% of agar agar.*

B. *With increasing conc. of 0.32% gold label gelatine.*

Adsorption of $SO_4$-ions.

Adsorption of $SO_4$-ions.

| Nature of sol. | N/50 $K_2SO_4$ added | Total | Physical | Chemical | Charge (e.s.u. × $10^5$) | N/50 $K_2SO_4$ added | Total | Physical | Chemical | Charge (e.s.u. × $10^5$) |
|---|---|---|---|---|---|---|---|---|---|---|
| Sol+water | 20.0 c.c. | 0.0438 g | 0.00351 g | 0.0403 g. | 5.17 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] agar+$H_2O$ | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 0.0439 | [illegible] | 0.0404 | 5.19 |
| Sol+10 c.c agar+$H_2O$ | 22.5 | 0.0435 | 0.00355 | 0.0400 | 5.14 | 22.5 | 0.0429 | 0.00355 | 0.0394 | 5.06 |
| [illegible] agar+$H_2O$ | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Sol+50 c.c agar+$H_2O$ | 22.5 | 0.0422 | 0.00358 | 0.0386 | 4.96 | 22.5 | 0.0407 | 0.00359 | 0.0371 | 4.77 |

From the results given in Tables II and V(A) it is seen that when methyl alcohol is added to the $As_2S_3$ and $Fe(OH)_3$ sols there is a slight lowering in the adsorption of the oppositely charged ions. This lowering in the adsorption may explain the sensitisation observed with methyl alcohol by Choudhury (*J. Phys. Chem.*, 1928, **28**, 1481). In the case of ethyl alcohol it is observed from Tables III(A) and V(B) that the adsorption increases but on adding larger amounts of ethyl alcohol it decreases but still remains greater than that by the original sol. From Tables III(B) and VI(A) it can be observed that in the case of agar agar the adsorption of the oppositely charged ion almost remains constant with a slight tendency to increase in lower concentrations of agar agar but in

# CHARGE AND STABILITY OF COLLOIDS. PART III. POTENTIOMETRIC TITRATIONS OF FERRIC HYDROXIDE SOL

By B. P. Yadava

The discrepancy in the results of Rabinowitsch and Weiser in the amounts of the counter-ions released on adding precipitating ions of varying valency to a ferric hydroxide sol has been investigated. It has been proved that the amount of the counter-ions released from a sol of ferric hydroxide depends on the purity of the sol. The quantity of the released chlorine from a ferric hydroxide sol gets smaller and smaller as the purity of the sol is increased by progressive dialysis. In the case of more impure sols the chlorine released is super-equivalent, whereas with increase of purity the quantity released is less than the chlorine equivalent of the added electrolyte.

Recently the mechanism of electrolyte coagulation of hydrophobic colloids has been studied by following the displacement of the counter-ions. Pauli (*Koll.-Chem. Beih.*, 1923, **17**, 256) used potentiometric titration method and has shown that in a ferric hydroxide sol, more and more of chlorine is set free on adding increasing quantity of the electrolyte. He measured the concentration of chlorine only at the end of the process, but Rabinowitsch and Kargin (*Z. physikal. Chem.*, 1928, **133**, 203) measured the chlorine concentration not only at the end but during the process of coagulation. They found that super-equivalent amount of chlorine is released on adding electrolytes. Weiser (*J. Phys. Chem.*, 1931, **35**, 1) allowed the sol and electrolyte mixtures to remain in contact for 24 hours before proceeding with the titrations. He used nitrate, sulphate, citrate and ferricyanide. In all these cases he found the displaced chlorine to be always less than the amount of the electrolyte added when expressed in chlorine equivalent.

It has been pointed out by Dhar (Dhar and co-workers, *J. Indian Chem. Soc.*, 1929, **6**, 31; 1932, **9**, 315,; 1933, **10**, 471) that the physical properties of a sol depend considerably on its purity. They have shown that if a sol contains a considerable amount of stabilising electrolyte it may behave abnormally on dilution, while a purer sample of it behaves normally. This means that the constitution of a sol changes with purity.

In view of the above the discrepancy in the observations of Rabinowitsch (*loc. cit.*) and Weiser (*loc. cit.*) appears ultimately to lie in the purity of the sol. It has been the object of this series of papers to estimate the amount of chlorine expelled from a sol of ferric hydroxide which was subjected to progressive dialysis.

## EXPERIMENTAL

Kahlbaum's ferric chloride (100 g.) was dissolved in freshly distilled water and diluted to about 4 litres. Dilute ammonia was added drop by drop, and after each addition of the drop of ammonia, the solution was thoroughly shaken. This process continued till the sol was just short of precipitation. The sol was filtered next day. A portion of the sol was set apart for potentiometric titrations from the original sol and the rest was kept for dialysis. Samples of sol were taken out from the dialysers after every sixth day. The concentrations of the original sol as well as those obtained by subsequent dialysis and the chlorine content of each sample were determined by the usual methods. A potentiometric method exactly similar to that of Weiser (*loc. cit.*) was used in order to avoid the uncertainty that may be present in Rabinowitsch's method.

## TABLE I

### Sol I

Conc. of $Fe_2O_3$ sol = 8·04 g./litre. Chlorine content = 0·312 g. ions/litre. *Purity of the sol. = 25·8. Temp. = 25°

| | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N-KNO₃ added. | π (volt). | $a_{Cl}$ × 10³ | Total. | displaced | equiv. to [NO₃] added. | (N/20) $K_2SO_4$ added. | π (volt). | $a_{Cl}$ × 10³. | Total. | displaced. | equiv. to [NO₃] added. | (N/100) K-citrate added. | π (volt). | $a_{Cl}$ × 10³. | Total. | displaced. | equiv. to [citrate] added |
| 0·0 c.c. | 0·0043 | 67·16 | 83·34 | 0·00 | 0 | 0 0 c.c. | 0·0043 | 67·16 | 83·34 | 0·00 | 0·0 | 0·0 c.c. | 0·0043 | 67·16 | 83·34 | 0·00 | 0·0 |
| 0·8 | 0·0041 | 67·68 | 84·28 | 0·94 | 40 | 0·4 | 0·0036 | 69·02 | 86·04 | 2·70 | 1·0 | 2·0 | 0·0035 | 69·28 | 86·16 | 2 82 | 1·0 |
| 1·6 | 0·0036 | 69·02 | 86·04 | 2·70 | 80 | 0·8 | 0·0027 | 71·47 | 89·33 | 5·99 | 2·0 | 4·0 | 0·0028 | 71·19 | 89·00 | 5·66 | 2·0 |
| 2·4 | 0·0031 | 70·37 | 87·97 | 4·63 | 120 | 1·2 | 0·0020 | 73 29 | 91·85 | 8·51 | 3·0 | 6·0 | 0·0022 | 72·89 | 91·23 | 7·89 | 3·0 |
| 3·2 | 0·0028 | 71·19 | 89·00 | 5·66 | 160 | 1·6 | 0·0015 | 74·89 | 93·95 | 10·61 | 4·0 | 8·0 | 0 0018 | 74·04 | 92·89 | 9·55 | 4·0 |
| 4·0 | 0 0024 | 72·32 | 90·53 | 7 19 | 200 | 2 0 | 0·0012 | 77·09 | 96·85 | 13·51 | 5·0 | 10·0 | 0·0013 | 75·47 | 94·83 | 11·49 | 5·0 |

## TABLE II

### Sol III.

Conc. of $Fe_2O_3$ sol = 7·36 g./litre. Chlorine content = 0·041 g. ions/litre. Purity of the sol = 179·5. Temp. = 25°.

| | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N-KNO₃ added. | π (volt). | $a_{Cl}$ × 10³. | Total. | displaced. | equiv. to [NO₃] added. | (N/20) $K_2SO_4$ added. | π (volt). | $a_{Cl}$ × 10³. | Total. | displaced. | equiv. to [SO₄] added. | (N/100) K-citrate added. | π (volt) | $a_{Cl}$ × 10³. | Total. | displaced. | equiv. to [citrate] added. |
| 0·0c.c. | 0·0333 | 21·71 | 24·54 | 0·00 | 0 | 0·0 c.c. | 0·0333 | 21·71 | 24·54 | 0·00 | 0 | 0·0 c.c. | 0·0333 | 21·71 | 24·54 | 0·00 | 0·0 c.c. |
| 0·4 | 0·0329 | 22·05 | 24·96 | 0·42 | 20 | 0·2 | 0·0326 | 22·32 | 25·30 | 0·76 | 0·5 | 2·0 | 0·0323 | 22·56 | 25·62 | 1·08 | 1·0 |
| 0·8 | 0·0327 | 22·22 | 25 16 | 0·62 | 40 | 0·4 | 0·0329 | 22·93 | 26·02 | 1·48 | 1·0 | 4·0 | 0·0314 | 23·77 | 26·65 | 2·11 | 2·0 |
| 1·2 | 0·0321 | 22·75 | 25·79 | 1·25 | 60 | 0·6 | 0·0311 | 23·65 | 26·87 | 2·33 | 1·5 | 5·0 | 0·0309 | 23·84 | 27·24 | 2·70 | 2·5 |
| 1·6 | 0·0317 | 23·11 | 26·22 | 1·68 | 80 | 1·0 | 0·0292 | 25·46 | 29·10 | 4·56 | 2·5 | 6·0 | 0·0304 | 24·31 | 27·81 | 3·27 | 3·0 |
| 2·5 | 0·0313 | 23·47 | 26·67 | 2·13 | 125 | 1·4 | 0·0278 | 26·89 | 30·92 | 6·38 | 3·5 | 8·0 | 0·0298 | 24·87 | 28·50 | 3·96 | 4·0 |

---

* Purity of the sol signifies the ratio [$Fe_2O_3$]/]Cl] in all the tables.

## TABLE III

### Sol IV

Conc. of $Fe_2O_3$ sol. = 6·85 g./litre. Chlorine content = 0·025 g. ions/litre. Purity = 274·0 Temp. = 25°

| | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ($N$/100) K-citrate added. | $\pi$ (volt). | $a_{cl} \times 10^3$. | Total. | displaced. | equiv. to [citrate] added. | ($N$/20) $K_2SO_4$ added. | $\pi$ (volt). | $a_{cl} \times 10^3$. | Total. | displaced. | equiv. to [$SO_4$] added. | $N$-$KNO_3$ added. | $\pi$ (volt). | $a_{cl} \times 10^3$. | Total | displaced. | equiv. to [$NO_3$] added. |
| 0·0 c.c. | 0·0728 | 4·66 | 5·01 | 0·06 | 0·00 | 0·0 c.c. | 0·0728 | 4·66 | 5·01 | 0·00 | 0·00 | 0·0 c.c. | 0·0728 | 4·66 | 5·01 | 0·00 | 0·0 |
| 1·0 | 0·0710 | 5·00 | 5·37 | 0·36 | 0·50 | 0·2 | 0·0702 | 5·16 | 5·55 | 0·54 | 0·50 | 0·4 | 0·0718 | 4·89 | 5·21 | 0·20 | 20 0 |
| 2 0 | 0·0695 | 5·30 | 5·71 | 0·70 | 1·00 | 0·4 | 0·0690 | 5·41 | 5·84 | 0·83 | 1·00 | 0·8 | 0·0706 | 5·08 | 5·46 | 0·45 | 40·0 |
| 3·0 | 0·0678 | 5·67 | 6·11 | 1·10 | 1·50 | 0·6 | 0·0654 | 6·22 | 6·72 | 1·17 | 1·50 | 1·2 | 0·0699 | 5·22 | 5·63 | 0·62 | 60·0 |
| 5·0 | 0·0666 | 5·93 | 6·41 | 1·40 | 2·00 | 0·9 | 0·0640 | 6·57 | 7·12 | 2·11 | 2·25 | 1·6 | 0·0684 | 5·53 | 5·97 | 0·96 | 80·0 |
| 7·0 | 0·0652 | 6·27 | 6·78 | 1·77 | 3·50 | 1·3 | 0·0611 | 7·35 | 7·99 | 2·98 | 3·25 | 2·4 | 0·0668 | 6·12 | 6·62 | 1·61 | 120·0 |

## TABLE IV

### Sol VI

Sol. conc. = 6·46 g./litre. Chlorine content = 0·01 g. ions/litre. Purity = 646·0. Temp. = 25°

| | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | | | | | [Cl] × 10³ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $N.KNO_3$ added. | $\pi$ (volt). | $a_{cl} \times 10^3$. | Total. | displaced. | equiv. to [$NO_3$] added. | ($N$/20) $K_2SO_4$ added. | $\pi$ (volt). | $a_{cl} \times 10^3$. | Total. | displaced. | equiv. to [$SO_4$] added. | ($N$/100) K-citrate added. | $\pi$ (volt). | $a_{cl} \times 10^3$ | Total. | displaced. | equiv. to [citrate] added. |
| 0·0 c.c. | 0·1065 | 1·26 | 1·28 | 0·00 | 0 | 0·0 c.c. | 0·1065 | 1·26 | 1·28 | 0·00 | 0·00 | 0·0 c.c. | 0·1065 | 1·26 | 1·28 | 0·00 | 0·0 |
| 0·2 | 0·0968 | 1·83 | 1·88 | 0·60 | 10 | 0·2 | 0·0963 | 1·87 | 1·91 | 0·63 | 0·50 | 1·0 | 0·0995 | 1·65 | 1·68 | 0·40 | 0·5 |
| 0·4 | 0·0920 | 2·21 | 2·27 | 0·99 | 20 | 0·4 | 0·0936 | 2·08 | 2·14 | 0·86 | 1·00 | 2·0 | 0·0985 | 1·72 | 1·76 | 0·48 | 1·0 |
| 0·6 | 0·0910 | 2·30 | 2·37 | 10·9 | 30 | 0·6 | 0·0913 | 2·27 | 2·35 | 1·07 | 1·50 | 3·0 | 0·0920 | 2·21 | 2·27 | 0·99 | 1·5 |
| 1·2 | 0·0902 | 2·37 | 2·45 | 1·17 | 60 | 0·8 | 0·0875 | 2·63 | 2·74 | 1·46 | 2·00 | 4·0 | 0·0900 | 2·39 | 2·46 | 1·18 | 2·0 |
| 1·6 | 0·0885 | 2·53 | 2·63 | 1·35 | 80 | 1·1 | 0·0847 | 2·93 | 3·09 | 1·81 | 2·75 | 6·0 | 0·0870 | 2·68 | 2·78 | 1·50 | 3·0 |

Potentiometric titrations were done by taking 10 c.c. of the sol of a particular sample in several stoppered bottles and to these were added electrolytes in varying concentrations starting from a certain minimum up to the coagulating concentration in a regular increasing order. The total volume of the sol and the electrolyte in each case was made up to 20 c.c. by adding the requisite amount of water to the electrolyte. The sol and the water-electrolyte mixtures were added uniformly so as to avoid any localised coagulation. Finally the sol-electrolyte mixtures were thoroughly shaken. To each of these bottles were added small doses of a pure sample of calomel, and the mixtures were left over for 24 hours to attain equilibrium. In a half element was placed the sol-electrolyte mixture, using platinum electrode which dipped in freshly distilled mercury, and the other half element was $N/10$-calomel electrode. The nozzles of both these half elements dipped in a vessel containing $N/10$-KCl solution.

A modified form of Nernst equation was used to calculate the activity of the displaced chlorine. This calculated value of the activity was converted into molar concentration by dividing it by the activity coefficient as read off from the graph obtained from the data of Lewis and Randal (*J. Amer. Chem. Soc.*, 1921, **43**, 1132). The amount of the electrolyte added is expressed in terms of the equivalent amount of chlorine. The results obtained with samples of different purity of the sol (purity signifies the ratio : $Fe_2O_3$ to Cl) are tabulated below and shown graphically in Figs. 1 and 2 with $KNO_3$ and $K_2SO_4$ only. For economy of space, the figure with K-citrate is not given but it is similar to Fig. 2 with $K_2SO_4$.

## DISCUSSION

From the above results it is clear that with the same sol the quantity of the displaced chlorine gets smaller and smaller as the sol becomes purer and purer even when the displaced chlorine is measured by one and the same method.

FIG. 1.

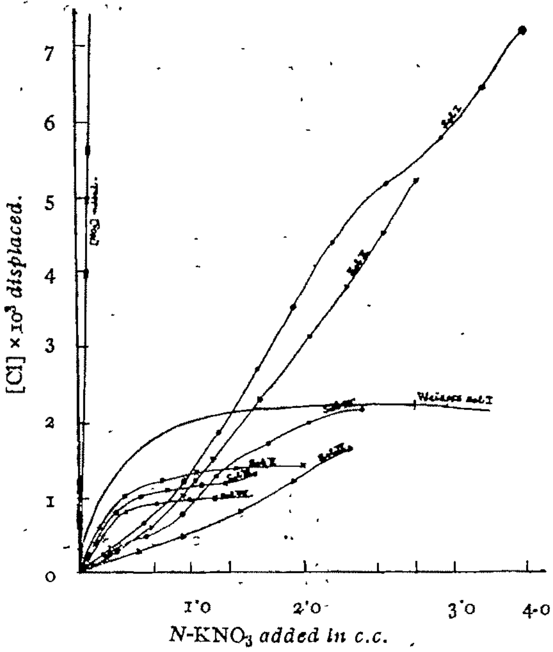
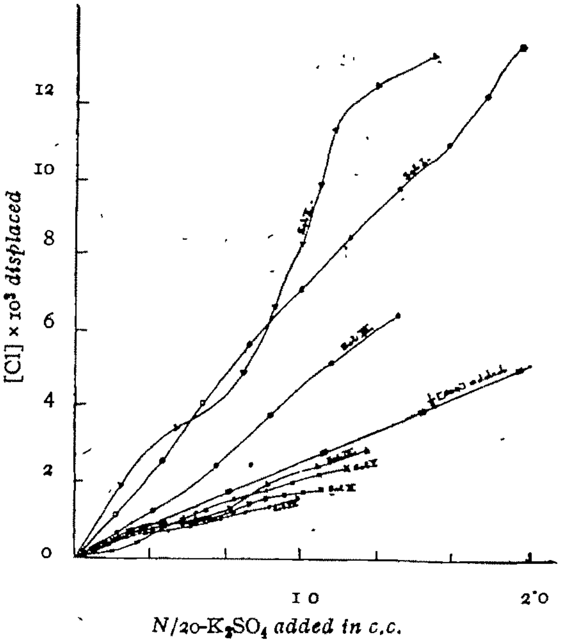


FIG. 2.



In the following table is given the relation between purity and the amount of chlorine displaced for the sols used in this paper (Table V). Detailed results of some of these are not given in order to economise space but the results obtained are plotted in Figs. 1 and 2.

TABLE V

| Sol. | Amount of $Fe_2O_3$ (g./litre). | Chlorine (g. mol/ litre). | Purity | Nature of Cl displaced |
|---|---|---|---|---|
| I | 8·04 | 0·312 | 25 8 | Super-equiv. |
| II | 7·54 | 0 095 | 79·4 | „ |
| III | 7·36 | 0·041 | 179·5 | „ |
| IV | 6·85 | 0·025 | 274·0 | < Equiv. |
| V. | 6·68 | 0·018 | 372·9 | „ |
| VI | 6·46 | 0·010 | 646·0 | „ |
| VII | 6·08 | 0·0085 | 715·4 | „ |

TABLE VI

| Sol. | Author. | $Fe_2O_3$ (g./litre) | Cl (g. mol/ litre). | Purity. | Nature of Cl displaced |
|---|---|---|---|---|---|
| I | Rabinowitsch | 8·71 | — | — | — |
| II | „ | 5 76 | 0·0254 | 226·8 | Super-equiv. |
| I | Weiser | 6·46 | 0·0158 | 408·7 | < Equiv. |
| II | „ | 6·92 | 0·0166 | 416·9. | „ |
| III | „ | 4·08 | 0·0047 | 868·2 | „ |

It is interesting to compare Table V with the one obtained from the results published by Rabinowitsch (*loc. cit.*) and Weiser (*loc. cit.*) as given in Table VI.

From Table VI it will be apparent that all the sols used by Weiser had a purity greater than the purity of the sol which begins to release chlorine ions less than the added quantity of the coagulating ions in the experiments recorded in the present communication.

From Table V it is clear that the sol used here behaves exactly in a similar manner to that of Weiser's as soon as it reaches a purity of 274·0, whereas sols of lesser purity release super-equivalent amounts of chlorine like that observed by Rabinowitsch.

It has been pointed out by Rabinowitsch that ageing of the sol also plays an important part. A more aged sol was observed by him to release a super-equivalent amount of chlorine. This behaviour very much resembles the behaviour of the impure sols used in this paper.

In sols of different degrees of purity used in this paper, a considerable amount of $KNO_3$ was necessary to effect coagulation but the released chlorine was considerably less than the added electrolyte (*cf.* Weiser, *loc. cit.*). Evidently the relation between the amount of chlorine released depends on the valency of the precipitating ion apart from the purity and the age of the sol.

The results with $KNO_3$ have been plotted in Fig. 1. From the curves it is apparent that the form bears a similarity to the form of the curves obtained with $K_2SO_4$ in Fig. 2. There is no real difference between the various curves. Weiser (*loc. cit.*) remarked that 'the form of the curve with $KNO_3$ was distinctly different from that for salts with multivalent precipitating ions'. Evidently the present work does not justify this. Weiser's statement is correct only when the purity of the sol is very high. (*cf.* curves for sols V, IV and VII and the one obtained with Weiser's sol I).

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# EXISTENCE OF SOME TRANSIENT HYDRATES

By Bholanath Ghosh

The presence of a large number of transient salt hydrates, with or without catalysts has been detected during the process of thermal dehydration of the hydrated salts by a differential thermocouple method.

It has been shown by the author (*J Indian Chem. Soc.*, 1941, **18**, 472) that the composition of hydrates can be fixed from a measurement of velocities of hydration and dehydration. Accurate experimentation shows that some hydrates, not otherwise traced, may appear occasionally in presence of catalysts. The nature of the nuclei developed in crystals during the process of dehydration has also been studied microscopically by the freeze-out method. The purpose of this paper is simply to trace some transient hydrates by a simple dehydration experiment, based on a differential thermo E.M.F. measurement principle. Such a method has already been used by Taylor and Klug (*J. Chem. Phys.*, 1936, **4**, 601) who found by differential thermo E.M.F. method a hydrate of composition $CuSO_4.4H_2O$ to appear during dehydration of copper sulphate pentahydrate which cannot be traced by any other method. Besides this, they give informations as regards the temperature at which water molecules in the crystal lattice change over from oscillatory to rotational state.

## EXPERIMENTAL

The hydrate to be investigated was put in a small bucket hung from a spring balance suspended in vacuum. Weight of the salt can thus be obtained by measurement of the distance between two fiducial marks of the balance. One junction of a thermocouple was inserted in the hydrate and the other junction kept in a bucket containing sodium chloride and the two junctions connected differentially. The two buckets were then simultaneously heated by keeping them together side by side in a common furnace whose temperature was slowly raised, with time. A galvanometer was connected in the thermocouple circuit to read the E.M.F. developed. Sudden changes in the deflection of the galvanometer indicate the formation of some hydrates transient (unstable) or stable. It may also indicate some sudden intrinsic changes in the nature of crystal lattice vibration or rotation. An extra thermocouple read the temperature of the furnace, to indicate the temperature at which the change took place. One junction of a supplementary thermocouple was kept embedded in the hydrate, the other junction being in ice, for direct determination of the temperature of the salt, as distinct from the temperature of the environment. All the thermocouples were made of very fine wires. The spring balance read the mass of the salt at the instant, where sudden changes were occuring in the E.M.F. of the differential couple. Sometimes the buckets were surrounded inside the furnace by freezing mixture kept in some suitable vessel. The heating current in the furnace was then put on, and increased slowly and the changes in mass and E.M.F. were measured as a function of time. This is necessary for studying low temperature changes in the hydrates during dehydration.

TABLE I

w stands for $H_2O$ and T for temp. in °C at which a particular hydrate or structure is being formed (given in bracket).
s, m, and l indicate respectively strong, medium and small.

| Hydrated salt. | Catalyst. | Hydrates and the corresponding w and T. | | Temp. of other intrinsic changes in crystals. | |
|---|---|---|---|---|---|
| | | Author's value. | Others' data. | Author's data | Others' value. |
| $CuSO_4, 5H_2O$ | — | 4½w(85), 4¼w(90); 4w(95) 3w(105); 2w(110); w(113) | 4w(96); 3w (102) (Ghosh, *loc. cit.*); w(113) (Taylor & Klug, *loc. cit.*) | 30°(s); 35·7(l); 55(s) | 29, 35, 53·7 |
| $CuSO_4, 5H_2O$ | Gold dust | 4w(93); 3¾w(98); 3w(102); 2w(106); 1½w(110); w(114); ½w(130) | — | 20°(l), 26(s); 36(m); 47(l) | — |
| $BeSO_4, 7H_2O$ | — | 6w(0), 5w(15); 4¾w(20); 4w(37) 3w(80), 2w(120); 1½w(151); 1w(180) | 6w(0) 4w(30); 2w(114); 1w(160); 0w(230) (Parsons, *J. Amer Chem. Soc.*, 1904, **26**, 721, *Science*, 1906, **25**, 402) | −10(s); −3(l); 7(m); 21(l) | — |
| $BeSO_4, 7H_2O$ | Sodium silicate | 6w(−2°). 5w(14), 4¾w(20); 4w(37); 3w(80), 2w(120); 1½w(151), 1w(180), ½w(201); 0w(260) | — | −14(l), −10(s); −4(l); +10(m); 27(m) | — |
| $Zn Cl_2, 4H_2O$ | — | 3½w(−30), 2¼w(−5); 2w(10), 1½w(26); 1w(56); ½w(112); 0w(180) | 4w; 3w; 2½w; 1w; ½w; (Mylius & Dietz, *Z. anorg. Chem.*, 1905, **44**, 217) | −26(s); −14(l); +16(s); +37(m) | — |
| $Zn Cl_2, 4H_2O$ | Cu dust | 3½w(−30), 3w(−26); 2½w(−10), 2w(0): 1½w(26); 1⅓w(40); 1w(60); ½w(120); 0w(180) | — | −24(s), −20(l); −12(s); 15(m); 39(l) | — |
| $ZnSO_4\ 6H_2O$ | — | 5½w(21); 5w(48); 4w(80); 3w(92); 2w(120); 1w(140); ½w(175) | 6w, 5w, 3½w, 3w, 2w, 1w (Mellor, "Treatise on Inorganic Chemistry," Vol. II) | 0(s); 14(l), 19(s); 37(l); 56(m) | — |
| $ZnSO_4, 6H_2O$ | Sodium phosphate | 5½w(20); 5w(46); 4½w(70); 4w(82); 3½w(86); 3w(95); 2½w(104); 2w(126); 1½w(135); 1w(146); ½w(180) | — | −2(s); +7(l); 15(s); 21(l); 36(s); 50(l); 58(m) | — |

## DISCUSSION

The data obtained have been represented in Table I. From inspection of the table it is evident that a large number of transient hydrates are formed, which are dynamically stable but which cannot be traced or isolated by any experiment of the static type. Besides these, a large number of changes in lattice vibrations have also been traced the nature of which seems to be unexplored as yet. The study of phase diagram of the ternary system consisting of the salt in question in presence of a second catalytic salt and water is likely to throw more light on this problem. The transient hydrates formed by the presence of finely divided metal, seems to be controlled by adsorption phenomena. In order that the catalysts may act effectively, the salt must be powdered very finely, and mixed intimately so that field of force of the metallic surface may influence the crystal formation in an effective manner.

The formation of these transient structures is perhaps first induced at the surface of the salts by the presence of foreign catalyst, which produces subsequently deeper changes in the salts undergoing dehydration and these seem to be transmitted to the interior so that the whole crystal system undergoes transient modifications and a new type of crystal structure is built up for a certain duration of time.

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# CHARGE AND STABILITY OF COLLOIDS. PART IV. POTENTIOMETRIC TITRATIONS OF ALUMINIUM HYDROXIDE SOL

By B. P. Yadava

Potentiometric titration method has been extended to aluminium hydroxide sol which was subjected to progressive dialysis to determine the amount of chlorine released from the counterpart of the double layer.

The amount of the counter-ion released depends on the purity of the sol. With impure sols super-equivalent amount of chlorine is released but as the purity of the sol increases, the released chlorine diminishes and becomes less than the equivalent of the electrolyte added after a particular purity has been reached.

The discrepancy in the results obtained by Rabinowitsch and by Weiser seems to be due to the different degrees of purity of the sols.

In the case of $KNO_3$ the displacement of the chlorine ions is considerably less than the added electrolyte with all sols irrespective of their purity.

In a previous communication of this series (*J. Indian Chem. Soc.*, 1943, **20**, 115) it was shown that a super-equivalent amount of chlorine was displaced from a ferric hydroxide sol, the purity of which had not reached a critical value above which an amount of chlorine less than the added electrolyte was released.

In those sols in which super-equivalent amount of chlorine was released, the method followed to estimate the chlorine was such that care was taken to avoid the production of localised coagulation of a portion of the sol. At the same time the sol-electrolyte mixtures were left over for 24 hours to attain equilibrium.

The work has been extended to aluminium hydroxide sol, prepared by the addition of ammonia to pure $AlCl_3$ and the chlorine displaced from samples of different purity of the same sol estimated.

## EXPERIMENTAL

The experimental procedure was exactly the same as given in Part III of this series of papers (*loc. cit.*). In this case aluminium hydroxide sol was prepared by dissolving about 100 g. of pure aluminium chloride in about four litres of freshly distilled water, and adding dilute ammonia drop by drop till the solution was just short of precipitation. The addition of the drops of ammonia was each time followed by a thorough shaking. The water-electrolyte mixtures were prepared separately, the electrolyte being taken in a regular increasing order such that the last concentration contained just the amount necessary to coagulate the sol within the stipulated time.

The same potentiometer and the reflecting galvanometer, which were used in the previous paper, were used in this paper as well. The experimental procedure was exactly similar to that used by Weiser (*J. Phys. Chem.*, 1931, **35**, 1368) in order to follow carefully the two precautions mentioned by him. The results obtained with samples of different purity* of the same sol of aluminium hydroxide are given in the following tables and shown graphically in Fig. 1, with potassium citrate. Figures with $KNO_3$ and $K_2SO_4$ are not given for economy of space, but are similar to that in Fig. 1.

## DISCUSSION

From the results given in Tables I-IV it is clear that in the case of aluminium hydroxide sol also, the quantity of chlorine displaced becomes smaller and smaller as the sol becomes purer and purer even when the displacement of chlorine ions is measured by one and the same method.

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* Purity of the sol in the tables signifies the ratio of $Al_2O_3$ to Cl.

TABLE I

*Experiments with sol I*

Conc. of the $Al_2O_3$ sol = 8·02 g./litre. $Cl_2$ content of the sol = 0·2284 g. ions/litre. Temp. = 25°. Purity = 35·1.

| | | | $[Cl]\times 10^3$. | | | | | | $[Cl]\times 10^3$. | | | | | | $[Cl]\times 10^3$. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *N*-$KNO_3$ added. | $\pi$ (volt). | $a_{Cl}\times 10^3$. | Total. | displaced. | equiv. to $[NO_3]$ added. | *N*/20-$K_2SO_4$ added. | $\pi$ (volt). | $a_{Cl}\times 10^3$. | Total. | displaced. | equiv. to $[SO_4]$ added. | *N*/100-K-citrate added. | $\pi$ (volt). | $a_{Cl}\times 10^3$. | Total | displaced. | equiv. to [citr.] added. |
| 0·0 c.c. | 0·0056 | 63·85 | 79·02 | 0·00 | 0 | 0·0 c.c | 0·0056 | 63·85 | 79·02 | 0·00 | 0·00 | 0·0 c.c. | 0·0056 | 63·85 | 79·02 | 0·00 | 0·0 |
| 2·0 | 0·0053 | 64·60 | 80·04 | 1·02 | 100 | 0·5 | 0·0049 | 65·60 | 81·40 | 2·38 | 1·25 | 2·0 | 0·0051 | 65·09 | 80·66 | 1·64 | 1·0 |
| 4·0 | 0·0048 | 65·86 | 81·60 | 2·58 | 200 | 1·0 | 0·0040 | 67·93 | 84·49 | 5·47 | 2·50 | 4·0 | 0·0043 | 67·16 | 83·34 | 4·32 | 2·0 |
| 6·0 | 0·0044 | 66·90 | 83·30 | 4·28 | 300 | 2·0 | 0·0034 | 69·55 | 86·62 | 7·60 | 5·00 | 6·0 | 0·0038 | 68·47 | 85·06 | 6·04 | 3·0 |
| 8·0 | 0·0041 | 67·68 | 84·38 | 5·36 | 400 | 3·0 | 0·0029 | 71·57 | 89·47 | 10·45 | 7·50 | 8·0 | 0·0026 | 71·75 | 89·69 | 7·67 | 4·0 |
| 10·0 | 0·0035 | 69·28 | 86·50 | 7·48 | 500 | 4·0 | 0·0022 | 72·89 | 91·33 | 12·31 | 10·00 | 10·0 | 0·0024 | 72·32 | 90·53 | 11·51 | 5·0 |

TABLE II

*Experiments with sol III*

Conc. of the $Al_2O_3$ sol = 7·56 g./litre. $Cl_2$ content of the sol = 0·1078 g. ion/litre. Temp. = 25°. Purity = 70·2.

| | | | $[Cl]\times 10^3$. | | | | | | $[Cl]\times 10^3$. | | | | | | $[Cl]\times 10^3$. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *N*-$KNO_3$ added. | $\pi$ (volt). | $a_{Cl}\times 10^3$. | Total. | displaced. | equiv. to $[NO_3]$ added. | *N*/20-$K_2SO_4$ added. | $\pi$ (volt). | $a_{Cl}\times 10^3$. | Total. | displaced. | equiv. to $[SO_4]$ added. | *N*/100-K-citrate added. | $\pi$ (volt). | $a_{Cl}\times 10^3$. | Total. | displaced. | equiv. to [citr.] added. |
| 0·0 c.c. | 0·0239 | 31·31 | 36·40 | 0·00 | 0 | 0·00c.c. | 0·0239 | 31·31 | 36·40 | 0·00 | 0 | 0·0 c.c. | 0·0239 | 31·31 | 36·40 | 0·00 | 0·00 |
| 2·0 | 0·0234 | 31·92 | 37·18 | 0·78 | 100 | 0·40 | 0·0231 | 32·30 | 37·62 | 1·22 | 1 | 2·0 | 0·0232 | 32·17 | 37·49 | 1·09 | 1·00 |
| 4·0 | 0·0228 | 32·68 | 38·14 | 1·74 | 200 | 0·80 | 0·0222 | 33·45 | 39·11 | 2·71 | 2 | 4·0 | 0·0225 | 33·06 | 38·62 | 2·22 | 2·00 |
| 6·0 | 0·0222 | 33·45 | 39·11 | 2·71 | 300 | 1·20 | 0·0215 | 34·37 | 40·30 | 3·90 | 3 | 6·0 | 0·0216 | 34·04 | 40·04 | 3·64 | 3·00 |
| 7·0 | 0·0218 | 33·97 | 39·77 | 3·33 | 350 | 1·60 | 0·0207 | 35·46 | 41·59 | 5·19 | 4 | 7·5 | 0·0208 | 35·32 | 41·41 | 5·01 | 3·75 |
| 8·0 | 0·0211 | 34·91 | 40·93 | 4·53 | 400 | 2·20 | 0·0202 | 36·16 | 42·44 | 6·04 | 5·5 | 8·5 | 0·0204 | 35·87 | 42·11 | 5·71 | 4·25 |

## TABLE III

*Experiments with sol IV*

Conc. of the $Al_2O_3$ sol=7·18 g./litre. $Cl_2$ content of the sol=0·042 g. ions/litre. Purity=167·5. Temp.=25°.

| | | | [Cl] × 10³. | | | | | | [Cl] × 10³. | | | | | | [Cl] × 10³. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *N*-$KNO_3$ added | $\pi$ (volt). | $a_{Cl} \times 10^3$. | Total. | dis-placed. | equiv. to $[NO_3]$ added. | *N*/20-$K_2SO_4$ added. | $\pi$ (volt). | $a_{Cl} \times 10^3$. | Total. | dis-placed. | eqiv. to $[SO_4]$ added. | *N*/20-K-citrate added. | $\pi$ (volt). | $a_{Cl} \times 10^3$. | Total. | dis-p'aced. | equiv to [citrate] added. |
| 0·0 c.c. | 0·0330 | 21·97 | 24·90 | 0·00 | 0 | 0·0 c.c. | 0·0330 | 21·97 | 24·90 | 0·00 | 0·0 | 0·0 c.c. | 0·0330 | 21·97 | 24·90 | 0·00 | 0·00 |
| 2·0 | 0·0322 | 22·66 | 25·75 | 0·85 | 100 | 0·4 | 0·0320 | 22·84 | 25·93 | 1·03 | 1·0 | 2·0 | 0·0323 | 22·57 | 25 63 | 0·74 | 1·00 |
| 4 0 | 0·0317 | 23·11 | 26·31 | 1·41 | 200 | 0·8 | 0·0311 | 23·65 | 26·88 | 1·98 | 2·0 | 4·0 | 0·0316 | 23·19 | 26·41 | 1·51 | 2·00 |
| 6 0 | 0·0308 | 23·92 | 27·30 | 2·40 | 300 | 1·2 | 0·0303 | 24·40 | 27·76 | 2·86 | 3·0 | 6·0 | 0·0310 | 23·74 | 27·09 | 2·19 | 3·00 |
| 7·0 | 0·0302 | 24·49 | 27·99 | 3·09 | 350 | 1·6 | 0·0295 | 25·17 | 28·80 | 3·90 | 4·0 | 7·0 | 0·0302 | 24·49 | 27·99 | 3·09 | 3·50 |
| 7·5 | 0·0295 | 25·17 | 28·80 | 3·90 | 375 | 2·0 | 0·0290 | 25·66 | 29·33 | 4·43 | 5·0 | 8·0 | 0·0293 | 25·37 | 29·06 | 4·16 | 4·00 |

## TABLE IV

*Experiments with sol VI*

Conc. of the $Al_2O_3$ sol=6·12 g./litre. $Cl_2$ content of the sol=0·01624 g. ions/litre. Purity=434·3. Temp.=25°.

| | | | [Cl] × 10³. | | | | | | [Cl] × 10³. | | | | | | [Cl] × 10³. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *N*-$KNO_3$ added. | $\pi$ (volt). | $a_{Cl} \times 10^3$. | Total. | dis-placed. | equiv. to $[NO_3]$ added. | *N*/20-$K_2SO_4$ added | $\pi$ (volt). | $a_{Cl} \times 10^3$. | Total. | dis-placed. | equiv. to $[SO_4]$ added. | *N*/100-K-citrate added. | $\pi$ (volt). | $a_{Cl} \times 10^3$. | Total | dis-placed. | eqiv. to [citrate] added. |
| 0·0 c.c. | 0·0820 | 3·26 | 3·29 | 0·00 | 0·0 | 0·00 | 0·0820 | 3·26 | 3·29 | 0·00 | 0·0 | 0·0 c.c. | 0·0820 | 3 26 | 3·29 | 0·00 | 0·00 |
| 1·0 | 0·0810 | 3·39 | 3·42 | 0·13 | 50·0 | 0·40 | 0·0819 | 3·27 | 3·30 | 0·01 | 1·0 | 1·0 | 0·0803 | 3·48 | 3·52 | 0·23 | 0·50 |
| 2·0 | 0·0805 | 3·45 | 3·49 | 0·20 | 100·0 | 0·80 | 0·0815 | 3·32 | 3·35 | 0·06 | 2·0 | 2·0 | 0·0780 | 3·81 | 3·85 | 0·56 | 1·00 |
| 3·0 | 0·0799 | 3·54 | 3·58 | 0·29 | 150·0 | 1·20 | 0·0810 | 3·39 | 3·42 | 0·13 | 3·0 | 3·0 | 0·0758 | 4·15 | 4·19 | 0·90 | 1·50 |
| 5·0 | 0·0795 | 3·59 | 3·64 | 0·35 | 250·0 | 1·40 | 0·0809 | 3·40 | 3·44 | 0·15 | 3·5 | 4·5 | 0·0740 | 4·45 | 4·50 | 1·21 | 2·25 |
| 6·0 | 0·0788 | 3·69 | 3·74 | 0·45 | 300·0 | 1·60 | 0·0801 | 3·51 | 3·55 | 0·26 | 4·0 | 5·5 | 0·0733 | 4·57 | 4·62 | 1·33 | 2·75 |

In Table V is given the relation between purity and chlorine displaced for the sols of different purity used. The detailed results for sols II, VI, VII are not given to economise space.

Here also it is found that the same sol begins to release less chlorine than the equivalent of the electrolyte added, as soon as its purity reaches a certain fixed point.

It is interesting to compare Table V with Table VI which gives the result obtained by Weiser (*loc. cit.*).

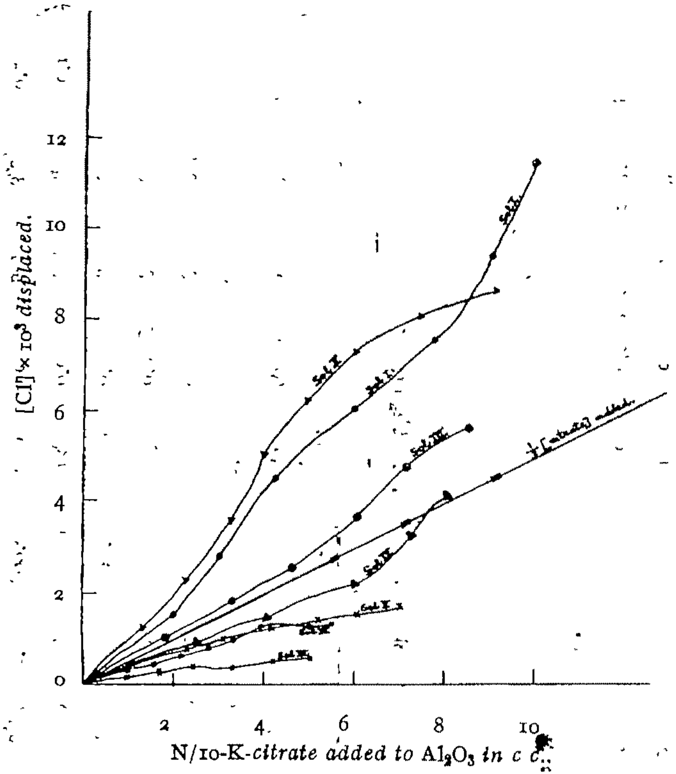
TABLE V

| Sol No. | Conc. of $Al_2O_3$ sol (g./litre). | $Cl_2$ content of the sol (g. ions/litre). | Purity of the sol. | Nature of displacement of chlorine. |
|---|---|---|---|---|
| I | 8·02 | 0·2284 | 35·10 | Super-equiv. |
| II | 7·92 | 0·1512 | 53·20 | ,, |
| III | 7 56 | 0·1078 | 70·20 | ,, |
| IV | 7·18 | 0 0420 | 167 50 | < Equiv |
| V | 6·56 | 0·0240 | 298·80 | ,, |
| VI | 6·12 | 0·0162 | 434·30 | ,, |
| VII | 5·88 | 0·0093 | 449·20 | ,, |

TABLE VI

| Sol No. | Conc of $Al_2O_3$ sol (g /litre). | $Cl_2$ content of the sol (g. ions/litre). | Purity of the sol. | Nature of displacement of chlorine. |
|---|---|---|---|---|
| I | 3·01 | 0·0160 | 188·1 | < Equiv. |
| II. | 4·12 | 0 0156 | 264 1 | ,, |
| III | 4·10 | 0·0164 | 250·0 | ,, |
| I | 5·08 | 0 0206 | 246·6 | ,, |
| II | 3·53 | 0 0268 | 131·5 | ,, |

It will be clear from Table VI that all the sols used by Weiser had far greater purity than those that give super-equivalent displacement of chlorine recorded in this paper.



From the results recorded in this series of papers it is now proved beyond reasonable experimental doubt that the super-equivalent displacement of chlorine does take place when a hydrous oxide sol, such as of iron or aluminium, is titrated with a multivalent anion provided the purity of these sols is below a certain number.

Weiser (*J. Phys. Chem.*, 1932, **36**, 2178) is of opinion that the super-equivalent displacement of chlorine observed by Rabinowitsch is a result of unsatisfactory experimental procedure which produces localised coagulation of a portion of the sol and does not allow time for equilibrium conditions to be approached. In experiments recorded in this series of papers (*loc. cit.*) great care was taken to avoid localised coagulation and also sufficient time was allowed to attain equilibrium, even then it has been found that some sols displace super-equivalent amount of chlorine. Weiser (*loc. cit.*) has studied the effect of time and concentration of the sol on the quantity of displaced chlorine and has found that with increase of time and dilution super-equivalent displacement of chlorine ceases. This is only true if the sol is sufficiently pure. Therefore to attribute the super-equivalent release of chlorine ions to a faulty experimental procedure as followed by Rabinowitsch, the original observer of this phenomenon, is not valid.

The author's sincere thanks are due to Dr. A. C. Chatterji for his valuable suggestions and guidance in this work.

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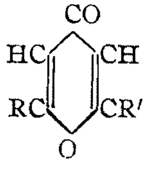
# PYRONE AND RELATED COMPOUNDS. PART III. ACTION OF BASES ON 2:6-DIHYDROXYPYRONE

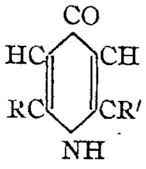
BY R. KAUSHAL

The reaction of aniline, ammonium acetate, pyridine and piperidine on dihydroxypyrone has been studied. Aniline brings about the fission of the pyrone ring and forms an anilic acid, a dianilide and in conjunction with zinc chloride forms *N*-phenyl-2:6-dihydroxypyridone. Ammonium acetate, pyridine and piperidine form oxonium compounds with the ring-oxygen. The basicity of the ring oxygen is discussed.

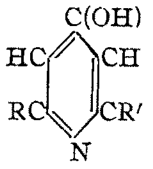
The pyrones (I) in general by the action of ammonia are converted into the corresponding pyridones (II) or the oxypyridines (III).



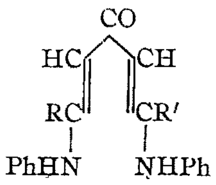
(I)



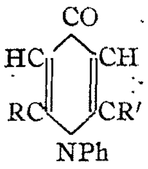
(II)



(III)



(IV)



(V)

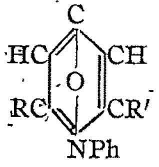
Dihydroxypyrone (I, R=R′=OH) does not give any isolable product by the action of ammonia but with alcoholic ammonia it gives the diammonium compound of 2:6-dihydroxypyridone (II, R=R′=OH, $2NH_3$. *J. Indian Chem. Soc.*, 1940, **17**, 138).

By the action of aniline on pyrone (I, R=R′=H) in dilute acetic acid Borsche and Bonacker (*Ber.*, 1921, **54B**, 2678) obtained dioxymethylene acetone dianilide (IV, R=R′=H) obviously by the rupture of the pyrone ring.

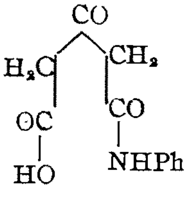
The dianilo-ketone is converted by hydrochloric acid, sodium ethylate or by distillation in vacuum into *N*-phenylpyridone (V, R=R′=H) (Smernoff, *Helv. Chim. Acta*, 1921, **4**, 599).

The action of aniline on 2 : 6-dihydroxy-4-pyrone is, therefore, expected to give some interesting results and to throw some light on the structures of *N*-substituted-4 pyridones.

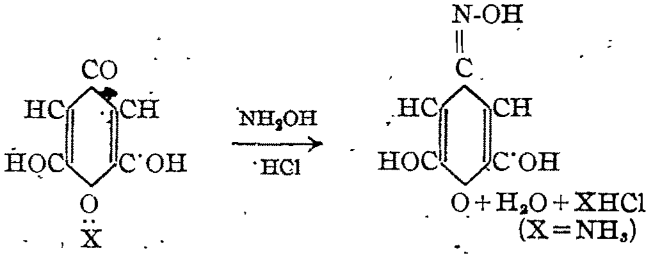
The dihydroxypyrone gives with aniline in chloroform solution, a crystalline monobasic acid of the composition $C_{11}H_{11}O_4N$, m.p. 120°. This must have been formed by the fission caused by the addition of the molecule of aniline and must be anilic acid of the structure (VII).



(VI)



(VII)



(VIII) (IX)

When, however, the dihydroxypyrone is boiled with excess of aniline and the excess removed with hydrochloric acid, another product of the composition $C_{17}H_{16}O_3N_2$, m.p. 157°, is obtained.

This is formed according to the equation, $C_5H_4O_4 + 2C_6H_5{\cdot}NH_2 = C_{17}H_{16}O_3N_2 + H_2O$ and therefore is the dianilide of acetone dicarboxylic acid (IV, R = R′ = OH or its keto form). The acetone dicarboxylic dianilide has been prepared by Besthorn and Garben (*Ber.*, 1900, **33**, 3443) from acetone dicarboxylic ester and aniline at 100°.

But aniline in conjunction with fused zinc chloride reacts with dihydroxypyrone in molecular proportions to give a third substance, m.p. 252°, of the composition $C_{11}H_9O_3N$. This third substance colours aqueous ferric chloride reddish violet on standing and is, therefore, 2 : 6-dihydroxy-1 phenyl-4 pyridone (V, R = R′ = OH).

It forms a nitrophenylhydrazone, m p. 184°, and reacts with acetic anhydride and sulphuric acid to give a product $C_{15}H_{13}O_5N$, which is the diacetate (V, $R = R' = O{\cdot}CO{\cdot}CH_3$). According to Smernoff the pyridone should have the structure (VI, R = R′ = OH) which is not likely in view of the fact that the substance forms a nitrophenylhydrazone (*cf.* Bedekar, Kaushal and Deshapande, *J. Indian Chem. Soc.*, 1935, **12**, 466).

The dihydroxypyrone and ammonium acetate at 0° yield an amorphous light white solid, m.p. 210°. Probably the ammonium acetate has converted the dihydroxypyrone into the corresponding pyridone (II, R = R′ = OH). On referring to the literature it was found that 2 : 6-dihydroxypyrone, which can also be regarded as trihydroxypyridine or triketopiperidine, is a yellowish sandy powder, m.p. 200-230°, and it is very soluble in hot water and forms a monooxime, m.p. 196° (*Ber.*, 1887, **20**, 2655).

The compound melting at 210° forms an oxime, m.p. 180°, and forms an acetate, m.p. 160°, which strikingly does not contain any nitrogen. All these compounds colour aqueous ferric chloride.

It, therefore, follows that ammonium acetate as expected has not been able to replace the oxygen of the ring by the-NH group. The analysis of the compound, melting at 210°, shows that it is only the ammonia addition product of the dihydroxypyrone (VIII, $X = NH_3$), in which the oxygen is quadrivalent and nitrogen pentavalent. On heating alone it evolves ammonia.

The analysis of the oxime agrees with $C_5H_5O_4N$ and is, therefore, the oxime of the dihydroxypyrone (IX) formed as shown above.

The analysis of the acetate melting at 160° corresponds to the formula $C_9H_8O_6$ and, therefore, is the diacetate of the dihydroxypyrone (I, $R = R' = O{\cdot}CO{\cdot}CH_3$). This is confirmed by an independent observation that the disodium compound of the dihydroxypyone, when heated with acetyl chloride, gives the same porduct.

This is not quite impossible in view of the fact that the pyrone structure (I, R = R′ = OH) is expected to impart to the compound basic properties, while the group $-C(OH) : CH-$, is expected to impart to the compound acidic properties. It has been shown by the author (*loc. cit.*) that the compound does not form oxonium salts with hydrochloric acid, chloroplatinic acid or picric acid. This is due to the presence of the negative -OH groups in the 2 : 6 positions, the oxygen behaves as though it were acidic and actually forms oxonium compound with bases like ammonia. This is further confirmed by the reaction of the dihydroxypyrone with pyridine or piperidine.

On mixing the dihydroxypyrone and pyridine, heat is evolved and a gummy solid separates which on purifying melts at 152°, and has the composition $C_{10}H_9O_4N$. This must have been formed by the addition of one molecule of pyridine to one of the dihydroxypyrone.

$$C_5H_4O_4 + C_5H_5N = C_{10}H_9O_4N$$

On gentle heating the compound $C_{10}H_9O_4N$ evolves pyridine and is, therefore, the oxonium compound (VIII, $X=NC_5H_5$). Similarly piperidine forms the oxonium compound (VIII, $X=NC_5H_{11}$). Like the former it evolves piperidine on gentle warming and colours aqueous ferric chloride violet.

Thus the basic function of the ring oxygen in 4-pyrones is dependent on the nature of the groups in the 2 : 6-positions. If R and R′ are positive organic radicals, the ring oxygen becomes strongly basic, *e.g.* pyrone (I, $R=R'=H$), dimethylpyrone (I, $R=R'=CH_3$) or diethylpyrone (I, $R=R'=C_2H_5$) are known to form well defined oxonium salts with acids (*cf.* Willstätter and Dummerer, *Ber.*, 1904, **37**, 3740 ; Collie and Tickle, *J. Chem.. Soc.*, 1899, **75**, 710 ; Deshapande *J. Indian Chem. Soc.*. 1932, **9**, 305). Here H, $CH_3$ or $C_2H_5$ are positive organic radicals. But when R and R′ are negative, the basic function of the ring oxygen is marred. For instance chelidonic acid or the ester (I, $R=R'=COOH$ or COOEt) are not known to form any oxonium salts with acids. In the case of the dihydroxypyrone the basic function of the ring oxygen is decreased to such an extent that it actually forms oxonium compounds with bases.

## EXPERIMENTAL

*Preparation of the Anilic Acid* (VII).—The reaction between aniline and the dihydroxypyrone takes place with or without the use of the solvent. Equimolecular quantities of the reactants were separately dissolved in chloroform and the solutions were mixed at the ordinary temperature. A slight evolution of heat was observed. On evaporating the solvent at the room temperature a viscous mass was left which on rubbing gradually solidified. This was put on a porous tile and the solid freed from the gum by rubbing with ether and hydrochloric acid. The anilic acid was crystallised from dilute alcohol as soft needles, m.p. 120-21°. (Found : C, 59·6 ; H, 4·9 ; N, 6·3. $C_{11}H_{11}O_4N$ requires C, 59·9 ; H, 4·9 ; N. 6·3 per cent).

*Preparation of the Dianilide* (IV, $R=R'=OH$).—The dihydroxypyrone (2 g.) was mixed with aniline (5 c.c.). After the initial reaction subsided, the mixture was boiled for 10 minutes when a portion on rubbing with hydrochloric acid gave a solid. It was then left in contact with hydrochloric acid to free it from aniline. The solid separating was well rubbed, filtered and washed with alcohol. It was then dried on a porous tile ; yield of the crude product 1 g. It crystallised from alcohol as thick small yellow needles, m.p. 157°. (Found : N, 9·0. $C_{17}H_{16}O_3N_2$ requires N, 9·4 per cent).

2 : *6-Dihydroxy-N-phenyl-4-pyridone* (V, $R=R'=OH$).—On addition of 1·5 g. of aniline (1 mol.) to 2 g. of dihydroxypyrone (1 mol.) a little frothing took place and heat was evolved. It was cooled and after addition of fused zinc chloride (5 g.) was refluxed for 10-15 minutes till the zinc chloride had gone into solution. On cooling and rubbing a solid separated which was filtered, washed and dried, yield 1 g. It was crystallised from absolute alcohol when it came out as almost colourless thick clusters of needles, m.p. 252° (darkening at 230°). (Found : N, 6·4. $C_{11}H_9O_3N$ requires N, 6·8 per cent).

The *nitrophenylhydrazone* was prepared by warming in hot water for 15 minutes equivalent quantities of the reacting substances in glacial acetic acid solution and diluting with water. On crystallisation from alcohol it came out as reddish brown prisms or globules, m.p. 184-85°.

The *diacetate* (V, $R=R'=O{\cdot}CO{\cdot}CH_3$) was prepared in the usual manner with acetic anhydride and traces of sulphuric acid. It was crystallised from alcohol and charcoal as long thin needles having a very pale yellow colour, m.p. 190°. (Found : C, 62·4 ; H, 4·4. $C_{15}H_{13}O_6N$ requires C, 62·7 ; H, 4·5 per cent).

*Action of Ammonium Acetate on 2 : 6-Dihydroxypyrone : Formation of the Oxonium Compound* (VIII, X=$NH_3$).—Ammonium acetate (10 g.) was dissolved in absolute alcohol (20 c.c.) and the dihydroxypyrone (4 g.) was gradually added to it under ice-cooling. The reaction started almost immediately for the dihydroxypyrone began to disappear and a white solid appeared in its place. This was left in an ice-chest for 24 hours and then filtered and washed with alcohol. Dried on a porous plate it melted at 200°, yield 3 g. It was crystallised from dilute alcohol from which it separated as clusters of small needles, m.p. 210° changing to a red liquid. (Found : N, 8·7. $C_6H_7O_4$ N, $H_2O$ requires N, 8·6 per cent).

The substance gives a beautiful violet colour to ferric chloride and evolves ammonia simply on heating.

*Formation of the Oxime* (IX).—To the hot aqueous solution of the compound (VIII, X=$NH_3$), on adding hydroxylamine hydrochloride solution a crystalline soft precipitate separated or it was obtained by boiling the solution of hydroxylamine hydrochloride and the compound (VIII, X=$NH_3$). This was crystallised from 90% alcohol as small microscopical prisms, m.p. 180° (decomp.). (Found : N, 9·6. $C_5H_5O_4N$ requires N, 9·8 per cent).

The oxime gives a violet colour to ferric chloride which deepens on standing.

*Formation of the Acetate* (I, R=R′=$OCOCH_3$).—To the compound (VIII, X=$NH_3$) acetic anhydride was added in excess and two drops of sulphuric acid. The mixture was heated for 5 minutes and poured on ice when after about 5 minutes the acetate separated as small crystalline shining plates having a very faint pinkish tinge, m.p. 160° to a red liquid. (Found : C, 50·3 ; H, 3·6. $C_9H_8O_6$ requires C, 50·9 ; H, 3·8 per cent)

This also gives a reddish violet colour to ferric chloride but only after standing for sometime.

On boiling the disodium dihydroxypyrone with excess of acetyl chloride in presence of a trace of sulphuric acid and pouring into water the same diacetate separated as a light pinkish solid, m.p. 159-60°.

*Reaction of Dihydroxypyrone and Pyridine : The Oxonium Compound* (VIII, X=$NC_5H_5$).—To well cooled pyridine was added the dihydroxypyrone when heat was evolved and a slight decomposition took place with evolution of carbon dioxide. On standing and rubbing the mass turned into a yellowish brown paste which was pressed on a porous tile. The resulting solid was crystallised from 80% alcohol as light needles, m.p. 152°. (Found : N, 6·8. $C_{10}H_9O_4N$ requires N, 6·8 per cent).

On gentle heating the compound darkened and evolved pyridine. It dissolves in water, the solution being slightly acid to litmus. It colours a aqueous ferric chloride violet.

*Reaction of Dihydroxypyrone and Piperidine : The Oxonium Compound* (VIII, X=$NC_5H_{11}$).—To well cooled piperidine, the dihydroxypyrone was added in slight excess and the mixture stirred well when gradually the pyrone went into solution and a thick jelly-like mass was formed. On rubbing it with benzene it became granular. It was filtered and pressed on a porous tile. Purified by washing it melted at 139°. It could be crystallised from benzene as small microscopical prisms having a very pale yellow colour, m.p. 139-40°. (Found : N, 6·4. $C_{10}H_{15}O_4N$ requires N, 6·6 per cent).

The substance is very soluble in water and evolves piperidine on gentle warming or heating. With aqueous ferric chloride it develops a beautiful violet colour at once.

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# MECHANISM OF FISSION OF ETHERS. PART I. FISSION OF AROMATIC ETHERS IN NON-AQUEOUS SOLVENTS

By S. P. Walvekar, N. L. Phalnikar and B. V. Bhide

Fission of aromatic ethers by HCl or HBr in various non-aqueous solvents has been studied and a mechanism of the reaction suggested.

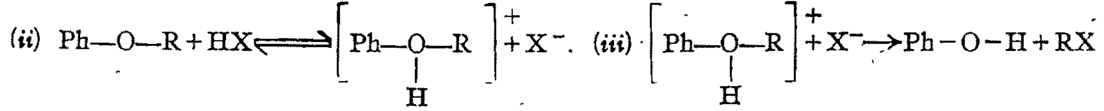
The kinetics of the reaction of halogen acids and the ethers has been studied in acetic and and formic acid solution by various workers (Ghaswalla and Donnan, *J. Chem. Soc.*, 1936, 1341; Birosel, *J. Amer. Chem. Soc.*, 1931, **56**, 1408). The reaction is represented by the following equation

$$\mathrm{Ph{-}O{-}R + HX \rightarrow Ph{-}O{-}H + RX.} \qquad \ldots \quad (i)$$

where R is an alkyl radical and X is Cl, Br or I.

This reaction has been termed as hydrolysis of ethers by most of the workers, however, as the equation shows, water does not take part in the reaction at all. The more appropriate term appears to be fission or cleavage of an ether by a halogen acid. Instead of hydrolysis, the term fission, therefore, has been used in the present work to represent the above reaction.

Ghaswalla and Donnan (*loc. cit.*) have studied the mechanism of fission of aromatic ethers by hydrogen bromide using 95% acetic acid as solvent. These authors have proposed the following mechanism :—



$$(ii)\ \mathrm{Ph{-}O{-}R + HX} \rightleftharpoons \left[\mathrm{Ph{-}\underset{\displaystyle H}{\underset{|}{O}}{-}R}\right]^{+} + \mathrm{X}^{-}. \quad (iii)\ \left[\mathrm{Ph{-}\underset{\displaystyle H}{\underset{|}{O}}{-}R}\right]^{+} + \mathrm{X}^{-} \rightarrow \mathrm{Ph-O-H+RX}$$

The reversible equation shown in (*ii*) is instantaneous and the oxonium complex is completely ionised. It will be observed therefore, that the reaction mechanism assumes the formation of the oxonium salt. Recently Meerwin, Hinz, Hofmann, Kroning and Pfeil (*J. prakt. Chem.*, 1937, *ii*, **147**, 257) have isolated salt like oxonium compounds with ethers. In these compounds the first three valencies of oxygen are co-valent and the fourth valency is electrovalent.

The object of the present work is to throw more light on the mechanism of fission of aromatic ethers by HCl or HBr. In the present work, therefore, the fission of aromatic ethers in various non-aqueous solvents has been studied and a mechanism has been proposed.

## EXPERIMENTAL

Anisole was purchased from Kahlbaum. The remaining ethers, *p*-chloroanisole, *p*-nitroanisole, *o*-nitroanisole and *p*-methylanisole were prepared by methylating the corresponding phenols according to standard methods. *p*-Bromoanisole was prepared according to the method of Birosel (*J. Amer. Chem. Soc.*, 1930, **52**, 1944). The ethers were purified by fractional distillation or crystallisation. All the purified samples of ethers had physical constants which agreed very well with the standard values.

The solvents, benzene, *n*-hexane, carbon tetrachloride and chloroform were carefully dried and purified by the usual methods.

Hydrogen chloride was prepared by the action concentrated sulphuric acid on pure ammonium chloride. Hydrogen bromide was prepared by gently warming pure potassium bromide with a syrupy mixture of phosphoric acid and phosphorus pentoxide according to the method of Fairbrother (*Trans. Faraday Soc.*, 1934, **30**, 862).

*Procedure.*—In these experiments the halogen acid was passed in the solution of the ether in the solvent in a tube till the necessary concentration was obtained and the tube was sealed and was heated at 70° in a thermostat. After a certain time the tube was taken out, chilled in ice and opened ; the contents were transferred to a flask containing distilled water. The halogen acid was titrated against standard sodium hydroxide. The unchanged ether was extracted with ether and washed with a slight excess of sodium hydroxide. The alkaline extract was used for the estimation of phenol as described by Ghaswalla and Donnan (*loc. cit.*). In some of the experiments the effect of the addition of small quantities of acetic acid, pyridine, dimethylaniline and aniline was studied. In these experiments and also in the case of anisidine the unchanged ether was weighed out and the extent of fission calculated. Experiments were carried out a stage further in the case of anisidine. It was thought that the following reaction

$$NH_2—Ph—OCH_3 + HBr \rightarrow NH_2PhBr + CH_3OH \quad \ldots \quad (iv)$$

might take place in preference to the usual reaction. The reaction mixture of hydrogen bromide and anisidine in carbon tetrachloride was acidified and the carbon tetrachloride was removed and washed with dilute hydrochloric acid. The aqueous solution and the washings were made alkaline and extracted with ether and the ether removed ; after drying the residue was weighed. It was found that this residue contained bromine This was attributed to the presence of *p*-bromoaniline formed according to the equation (*iv*). Analysis showed, however, that *p*-bromoaniline was present to the extent of 1% only, the rest being anisidine. The experiment shows that the reaction (*iv*) takes place only to a small extent.

In these experiments it was difficult to maintain exactly the same concentration of the halogen acid in all the experiments, and therefore assuming a proportionality between the concentration of the halogen acid and the percentage fission, all the results for percentage fission have been calculated for a particular concentration of the halogen acid as indicated in the tables. Attempt was made, however, to maintain the concentration of the halogen acid as near as possible to the concentration mentioned in the table. The error in the estimation of phenols generated is about 0·5%. Results of these experiments and a discussion thereon are given below.

## RESULTS

The following tables give the results of the fission of ethers with hydrogen chloride and hydrogen bromide in carbon tetrachloride and hexane solutions.

TABLE I

Solvent = $CCl_4$. Reagent = HCl (0·1 *M*).

| Ether (0·1 *M*) | Temp. | Time. | % Fission. |
|---|---|---|---|
| Anisole | 70° | 10 hours | 0·90 |
| Anisole | 70° | 50 | 0·80 |
| Anisole | 70° | 40 | 0·70 |
| Anisole (0·5 *M*) | 25-30° | 5 months | 0·90 |
| *p*-Methylanisole | 70° | 10 hours | 0 50 |
| *p*-Nitroanisole | 70° | 10 | 0·35 |
| *p*-Bromoanisole | 70° | 10 | 0·45 |
| *p*-Chloroanisole | 70° | 10 | 0·35 |

TABLE II

Solvent = $CCl_4$. Reagent = HBr (0·5 *M*).

| Ether (0·1 *M*) | Temp. | Time. | % Fission. |
|---|---|---|---|
| Anisole | 70° | 9 hours | 0·96 |
| *p*-Chloroanisole | ,, | ,, | 0·55 |
| *p*-Methylanisole | ,, | ,, | 1·20 |
| *p*-Bromoanisole | ,, | ,, | 0.75 |
| *p*-Nitroanisole | ,, | ,, | 0·43 |
| *o*-Nitroanisole | ,, | ,, | 0·57 |

TABLE III

Solvent = *n*-Hexane.

| Reagent. | Ether. | Temp. | Time. | % Fission |
|---|---|---|---|---|
| HCl (0·5 *M*) | Anisole | 25-30° | 3½ months | 1·00 |
| HBr (0·5 *M*) | Anisole | 70° | 10 hours | 0·40 |

It will be observed from the above tables that the fission of anisole by hydrogen chloride was less than 1% even after 50 hours at 70° in sealed tubes. The fission did not proceed further even on keeping the reaction mixture for five months at room temperature (25-30°) (Table I). The observed fission (1%) may be due to experimental errors in the estimations of free phenol generated, since the fission is small (about 0·5%) in the case of all the others studied in carbon tetrachloride and *n*-hexane solutions.

Experiments (Table II) were tried with hydrogen bromide but fission was again under 1%. It may, therefore, be concluded that the fission of ethers does not take place appreciably in *n*-hexane and carbon tetrachloride solutions in the presence of hydrogen chloride or bromide.

The halogen acids are not ionised in carbon tetrachloride or *n*-hexane, and hence the results given in the above table show that unionised HCl or HBr is unable to bring about the fission of ethers in these solvents.

These important results showed that the mechanism of the reaction might be similar to acid base catalysed reactions. Working from analogy (*e.g.*, mutarotation of glucose by Lowry) the effect of the presence of bases in these solvents was studied.

In the first instance the effect of introduction of pyridine in the reaction mixture was tried and the results were according to expectations (Table IV). The increase in reaction took place appreciably but to a small extent in anisole with hydrogen chloride, therefore; further experiments were carried out with hydrogen bromide instead of hydrogen chloride. The following table summarises the results.

TABLE IV

Base = 5% Pyridine. Reagent = *M*-HBr. Temp. = 70°. Time = 10 hr. Solvent = $CCl_4$.

| Ether | Anisole | *p*-Chloro- | *p*-Bromo- | *p*-Methyl- | *o*-Nitro- | *p*-Nitro- |
|---|---|---|---|---|---|---|
| % Fission... | 37·12 (*2·68) | 20·08 | 6·52 | 4·42 | 1·54 | 4·45 |
| | (28·73**) | — | — | — | — | — |

* Figure denotes fission with 1*M*-HCl for 11 hours.

** The figure denotes fission with 1*M*-HBr for 10 hours in *n*-hexane.

Further in order to make the experiments more comprehensive the effect of other bases like dimethylaniline and aniline was also studied and the following table shows the results.

TABLE V

Solvent = $CCl_4$. Reagent = 1·0*M*-HBr. Temp. = 70°.

| Ether (0·5 *M*). | Base (5%) | Time. | % Fission. |
|---|---|---|---|
| Anisole | Dimethylaniline | 10 hours | 78·39 |
| Anisole | Aniline | ,, | 64·79 |
| Anisidine | — | 9 hours | 79·37 |

The effect of pyridine on the extent of fission is very striking. Thus in the case of anisole the fission by 0·5*M*-hydrogen bromide was about 1% in carbon tetrachloride (Table II) while in the presence of pyridine the fission was nearly 37·1% with 1·0 *M*-hydrogen bromide (Table IV). In *n*-hexane likewise the fission increased from 0·4 to 28·7% under the same conditions (Table IV). The results with dimethylaniline and aniline are similar (Table V). These experiments indicate that the presence of a base is an important factor in the reaction.

Ghaswalla and Donnan (*loc. cit.*) showed that the reaction took place easily in 95% acetic acid as solvent. In this case the function of the base in the reaction may be attributed to acetic acid.

In order to see the effect of acetic acid in small quantities on the extent of fission of the ethers and also to study the extent of fission in glacial acetic acid, several experiments were carried out and the results are given in the following tables.

TABLE VI

Solvent = CCl$_4$. Reagent = 0·5 *M*-HBr. Temp. = 70°. Time = 6 hours.
Conc. of acetic acid = 5%.

| Ether (0·5*M*) | ... Anisole | *p*-Chloro- | *p*-Bromo- | *p*-Methyl- | *o*-Nitro- | *p*-Nitro- |
|---|---|---|---|---|---|---|
| % Fission | ... 9·26 | 3·85 | 3·28 | 6·62 | 3·77 | 2·04 |

TABLE VII

Anisole (0·5*M*).

Solvent = acetic acid (glacial).

| Reagent. | Temp. | Time. | % Fission |
|---|---|---|---|
| HCl (0·37*N*) | 25-30° | 3½ months | 12·24 |
| HCl (0·23*N*) | 70° | 42 hours | 15·15 |
| HBr (1·04*N*) | 70° | 10 hours | 96·85 |
| Solvent = 95% acetic acid. | | | |
| HCl (0·24*N*) | 25-30° | 5 months | 18·64 |

From the above tables it will be observed that due to the presence of acetic acid the extent of fission increases from 1 to 9·2% in the case of anisole in carbon tetrachloride (*cf.* Tables II & VI). Similarly it will be seen that the reaction takes place to an appreciable extent in the case of glacial acetic acid and in 95% acetic acid. It has already been indicated that the presence of a base is an important factor in the fission of the ether. In this case also the accelerating effect due to the presence of acetic acid can be attributed to the acetic acid functioning as a base. On the Lowry and Bronsted theory of acids and bases, the anion is regarded as a base (proton acceptor) but in carbon tetrachloride or in hexane solution, acetic acid will not ionise at all. Hence the only way in which acetic acid can act as the base is by combining with the proton belonging to the halogen acid (solvation)

$$\mathrm{HX} + \mathrm{CH_3{-}COOH} \rightarrow \mathrm{CH_3{-}COOH_2^+} + \mathrm{X^-}$$

This type of solvation is supported by the very high solubility of hydrogen chloride and hydrogen bromide in acetic acid.

A few experiments have been carried out in non-hydroxylic solvents having different dielectric constants such as nitrobenzene, chloroform, etc. The following tables give the results.

TABLE VIII

*Fission of ethers in diffeıent solvents*

Temp. = 70°.

A. With 1·0*M*-HBr. B. With 1·5*M*-HBr + 5% pyridine.

| | A. | | | | B. | |
|---|---|---|---|---|---|---|
| | | Percentage fission of | | | | % Fission |
| Solvent. | D.C. | anisole. | *p*-methylanisole. | nitroanisole. | D.C. | of anisole. |
| Nitrobenzene | 36·45 | 65 7 | 42·0 | 3·5 | 36·45 | 99·79 |
| Chloroform | 5·14 | 29·9 | 38·8 | 2·25 | 5·14 | 54 67 |
| Chlorobenzene | 5·36 | 3·65 | 3·89 | 1·8 | 5 36 | 31·12 |
| Acetic acid | 9·0 | 71·66 | 50·47 | — | 9·0 | 96·45 |

It will be observed from the above table that the extent of fission is greater in the solvent with higher dielectric constant (D.C.) and the reaction proceeds still further with the addition of a catalyst like pyridine.

The above experimental observations bring out the following points :—

(*i*) Hydrogen chloride or bromide are co-valent compounds in non-polar solvents and under these conditions the reaction between the acid and the aromaric ethers does not take place.

(*ii*) The reaction can take place in non-polar solvents if a base like pyridine, dimethylaniline or aniline is present. The base forms a salt with the halogen acid and the co-valent link between the halogen and the hydrogen atom changes into an electrovalent link, the hydrogen atom joining itself to the base. A hydroxylic solvent like acetic acid can also function as a base by the solvation of the proton of the halogen acid.

(*iii*) Hydrogen chloride and hydrogen bromide react very easily with ethers in a polar solvent like acetic acid, formic acic, propionic acid, nitrobenzene, chloroform, etc. (*cf.* Ghaswalla and Donnan *loc. cit.* Birosel *loc. cit.* Bapat and Kolhatkar, *J. Univ. Bom.*, 1938, III, **8**, 157).

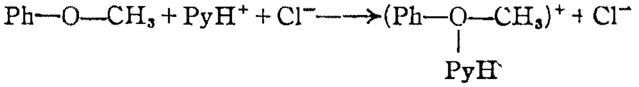
(*iv*) The halogen acids can react with the aromatic ethers only when the bond between the hydrogen and the halogen changes from co-valent to electrovalent type.

This can be achieved by the presence of (*a*) a proton acceptor like pyridine, aniline, dimethylaniline or (*b*) hydroxylic solvents like acetic acid, or, (*c*) a solvent with a high dielectric constant like nitrobenzene.

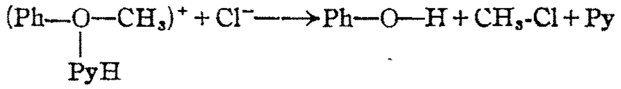
The following mechanism can therefore be proposed for the fission of ethers by halogen acids :—

(*a*) Fission of ethers in presence of a base (pyridine = Py).

$$Py + HCl \longrightarrow Py\dot{H}Cl$$



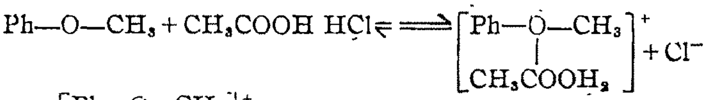
$$Ph{-}O{-}CH_3 + PyH^+ + Cl^- \longrightarrow (Ph{-}\underset{\underset{\textstyle PyH^{\cdot}}{|}}{O}{-}CH_3)^+ + Cl^- \qquad \ldots (1)$$



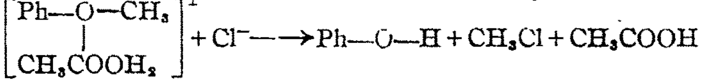
$$(Ph{-}\underset{\underset{\textstyle PyH}{|}}{O}{-}CH_3)^+ + Cl^- \longrightarrow Ph{-}O{-}H + CH_3\text{-}Cl + Py \qquad \ldots (2)$$

(*b*) Fission of ethers in the presence of a hydroxylic solvent like acetic acid.

$$CH_3{-}COOH + HCl \longrightarrow CH_3{-}COOH\ HCl$$



$$Ph{-}O{-}CH_3 + CH_3COOH\ HCl \rightleftharpoons \begin{bmatrix} Ph{-}\underset{|}{O}{-}CH_3 \\ CH_3COOH_2 \end{bmatrix}^+ + Cl^- \qquad \ldots (3)$$



$$\begin{bmatrix} Ph{-}\underset{|}{O}{-}CH_3 \\ CH_3COOH_2 \end{bmatrix}^+ + Cl^- \longrightarrow Ph{-}O{-}H + CH_3Cl + CH_3COOH \qquad \ldots (4)$$

Reaction (1) and (2) are reversible and rapid. While reactions (3) and (4) are slow and determine the rate of the reaction. Mechanism proposed in (*b*) requires some remarks. Acetic acid acts as a base (proton acceptor) according to the following equation :—

$$CH_3COOH + HCl \rightarrow [CH_3COOH_2]^+ + Cl^-$$

This equilibrium cannot go very far to the right. The halogen acid will therefore be weak, in the sense that the extent of ionisation and conductance will be smaller than those for the corresponding acid in water ; even acids like perchloric acid which are highly ionised in water appear to be dissociated to a small extent in acetic acid. It is a very striking fact, however, that the hydrogen ion activity in such solutions is exceptionally high, much higher than in aqueous solutions so that they have been termed *superacids* (Hall and Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 3047, 3062).

This activity is attributed to the fact that the ($CH_3COOH_2^+$) ion has a marked tendency to loose a proton. The same observation applies to formic acid as well. The high proton activity well enable the formation of the oxonium salt and hence the great ease with which the others are split up in acetic, formic or propionic acids as medium is accounted for.

The mechanism is not different from the one proposed by Ghaswalla and Donnan (*loc. cit.*) and is not in conflict with the kinetic measurements carried out by them. These authors, however, did not consider the rôle of the solvent functioning as a base in the mechanism of the reaction.

Our experiments on the fission of anisole in nitrobenzene and other solvents deserve some remarks. It is well known that hydrogen chloride or bromide is not highly ionised in these solvents. The low conductivity must be due to the formation of ion pairs. Ionisation of the halogen acid in solvents like nitrobenzene and chloroform enables oxonium salt formation and therefore fission can occur. In hexane and carbon tetrachloride the halogen acids are not at all ionised. In nitrobenzene the fission is greater than in chloroform because of its higher dielectric constant. Chlorobenzene and chloroform have the same dielectric constants but the fission takes place to a much greater extent in chloroform than in chlorobenzene. It appears, therefore, that apart from the dielectric constant the solvent can have its own specific effect.

In the proposed mechanism it will be observed that the rate determining factor is the reaction between the halogen anion and the alkyl group ($CH_3$). The introduction of a negative group in the phenoxy radical will make the bond between the alkyl and the phenoxy radical stronger as the alkyl group is electro-positive. The rate of the reaction between the alkyl group and the halogen ion will be diminished. The observed order of fission $H > Cl > Br > NO_2$ due to the influence of groups introduced in the phenoxy radical (Ghaswalla and Donánn, *loc. cit.*) bears out this point.

The results of fission of *p*-methylanisole show some peculiar results. Ghaswalla and Donnan (*loc. cit.*) found that the rate of fission was very great with *p*-methylanisole ($k = 102 \times 10^{-4}$) as compared with anisole ($k = 71{\cdot}40 \times 10^{-4}$). Our results in the case of HBr and pyridine in carbon tetrachloride solution (Table IV), HBr and acetic acid in carbon tetrachloride solution (Table VI) and HBr in nitrobenzene (Table VIII) show greater fission of anisole than that of *p*-methylanisole, while in chloroform (Table VIII) the order is reversed.

Further work is in progress.

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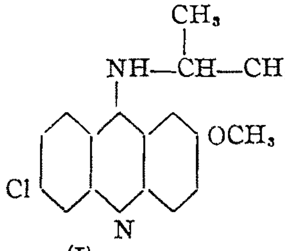
# CHEMOTHERAPY OF MALARIA

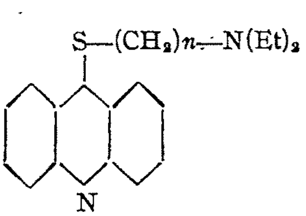
By S. J. Das-Gupta

The preparation of some 5-thiolacridine derivatives is described.

Of all the acridine derivatives, those which contain a dialkylamino-alkylamino group in 5-position possess strongest antimalarial properties. Atebrin (I), which is a compound of this type, is very effectively used in malaria. It possesses strong antiseptic action against all asexual forms of malarial parasites (Kikuth, *Deut. Med. Wochs.*, 1932, **68**, 530; Magidson and Grigorowski, *Ber.*, 1936, **69**, 396; Mauss and Mietzsch, *Klin. Wosch.*, **12**, 1276).



(I)



(II)

Recently the author described a number of 5-thiolacridine compounds which may be regarded as the sulphur analogues of 5-aminoacridines (*J. Indian Chem. Soc.*, 1940, **17**, 244). From an examination of the compounds of type (I) it is evident that the addition of a dialkylaminoalkyl group to the 5-aminoacridines develops remarkable antimalarial properties. So it was contemplated that the addition of the same group *i.e.* dialkylaminoalkyl to the 5-thiolacridines may develop antimalarial or other chemotherapeutic properties. Hence an investigation has been undertaken to synthesise a number of compounds of type (II) and to study their chemotherapeutic properties. Several of such compounds have already been prepared and as expected have been found to possess strong antiseptic action against paramecia. The experimental results on paramecia will be described elsewhere.

The compounds are low melting and have, therefore, been isolated as hydrochlorides which are highly soluble in water. The molecular weights of these compounds are favourable for an antimalarial drug (*cf.* Slotta and Behnisch, *Ber.*, 1935, **68**, 754).

## EXPERIMENTAL

*2-Chloro-7-methoxy-5-(β-diethylaminoethyl) thioacridine.*—2 G. of 2-chloro-7-methoxy-5-thiolacridine (Das-Gupta, *loc. cit*) was heated with β-diethylaminoethyl bromide hydrobromide (5 g.) in phenol (10 g.) containing 3-4 g. of sodium hydroxide 100-110° for 3 hours. The mixture was poured into dilute sodium hydroxide solution. The alkaline solution was extracted with ether. The ethereal solution was extracted with dilute acetic acid. The acetic acid solution after being shaken with ether, was made alkaline with sodium hydroxide solution and again extracted with ether. The ether extract was washed with water and evaporated, when a viscous liquid was obtained. This was treated with concentrated hydrochloric acid in cold. On concentrating the acid solution in vacuum small orange-yellow rectangular needles of the dihydrochloride were obtained. This was further crystallised from alcohol-ether mixture, m.p. 225°. (Found : N, 6·4 ; Cl, 23·6. $C_{20}H_{23}ON_2ClS$, 2HCl requires N, 6·25 ; Cl, 23·8 per cent).

*7-Methoxy-5-(β-diethylaminoethyl)thioacridine* was prepared from 7-methoxy-5-thiolacridine and β-diethylaminoethyl bromide hydrobromide, exactly in the same way as in the previous case. The dihydrochloride was finally obtained as orange-yellow needles, m.p. 209-10°. (Found : Cl, 17·14 ; S, 7·96. $C_{20}H_{24}ON_2S$, 2HCl requires, Cl, 17·19 ; S, 7·74 per cent).

*2-Chloro-7-methoxy-5 (γ-diethylaminopropyl)thioacridine* was prepared from 2-chloro-7-methoxy-5-thiolacridine (1 mol.) and γ-diethylaminopropyl chloride (1.2 mol.) by heating in phenol at 110-120° for several hours. After treatment of the reaction mixture as in the previous cases, the dihydrochloride was obtained as orange-yellow needles from alcohol-ether mixture, m.p. 195-97°. (Found : N, 5·89. $C_{21}H_{25}ON_2ClS$, 2 HCl requires N, 6·07 per cent).

*7-Methoxy-5-(γ-diethylaminopropyl)thioacridine* was prepared from 7-methoxy-5-thiolacridine and γ-diethylaminopropyl chloride in the same way as before and the dihydrochloride was obtained as orange-yellow needles, m.p. 180-81°. (Found : N, 6·34. $C_{21}H_{26}ON_2S$, 2 HCl requires N, 6·56 per cent).

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# SEPARATION OF COBALT FROM NICKEL USING ACETONE AS A SOLVENT

By M. M. Tillu

Separation of cobalt from nickel has been effected by using acetone as a solvent. The method is based upon the principle that cobalt chloride is highly soluble in acetone while nickel chloride is insoluble in the same solvent.

In continuation of our work on the separation of calcium from strontium using acetone as a solvent (Tillu and Telang, *J. Indian Chem. Soc.*, 1942, **19**, 231), it has been found out that acetone can also be used to separate cobalt from nickel.

In the estimation of cobalt the main difficulty is to obtain cobalt in the form of its compound entirely free from nickel (Friend, "Text Book of Inorganic Chemistry", Vol. IX, Part I, p. 75). Although many methods of their separation are found in literature, they are either complicated, or involve the use of very costly and complex organic compounds, which cannot be easily accessible in the purest condition. Moreover, they are not without their limitations. This new method of separation is simple, cheaper, and is applicable irrespective of the amount of nickel present.

Nickel chloride is insoluble in acetone while cobalt chloride is highly soluble. It follows therefore that the two elements should be present in the mixture as dry chlorides. If they are not initially present as chlorides they have to be converted into dry chlorides. Thus after separation by this method cobalt or nickel can be estimated by the usual method.

## EXPERIMENTAL

The order of solubility of nickel chloride in acetone as found by the author at 35° is 1 part in 16000 parts of acetone. Cobalt chloride is highly soluble.

Various mixtures of cobalt chloride and nickel chloride were prepared in aqueous solution and the results of analysis have been recorded in the accompanying table.

A known quantity of cobalt chloride solution (about 2%) was taken in a weighing bottle and evaporated to dryness at 110°, the weight of the residue corresponding to the amount of cobalt chloride taken (Friend, *ibid.*, p. 39). To this residue of cobalt chloride ($CoCl_2$, $H_2O$) again a known quantity of nickel chloride solution in dilute hydrochloric acid (about 2%) was added and evaporated to dryness at 110° (Ditte, *Ann. Chim. Phys.*, 1881, *v*, **22**, 551). The weight of this residue less the weight of cobalt chloride taken gives the weight of nickel chloride ($NiCl_2$, $H_2O$).

The mixture of dry chlorides was prepared by evaporation at 110°. Cobalt chloride was extracted with acetone from nickel chloride and the filtration was done through a sintered glass crucible. The acetone solution was evaporated to dryness in a previously weighed platinum dish and the residual cobalt chloride was further dried at 110°, and weighed as such. The nickel chloride left behind after extraction in the sintered glass crucible was dried and weighed.

TABLE I

| Mixture No | $CoCl_2$, $H_2O$ | | $NiCl_2$, $H_2O$ | |
|---|---|---|---|---|
| | Actual. | Found. | Actual. | Found. |
| I | 0·1300 | 0·1290 | 0·1700 | 0·1713 |
| II | 0·0663 | 0·0658 | 0·1720 | 0·1715 |
| III | 0 1324 | 0·1320 | 0·0844 | 0·0840 |
| IV | 0·0668 | 0·0653 | 0·2545 | 0·2535 |
| V | 0·1964 | 0·1970 | 0·0832 | 0·0838 |
| VI | 0 0656 | 0·0646 | 0·3450 | 0·3446 |
| VII | 0·2652 | 0·2648 | 0·0838 | 0·0832 |
| VIII | 0·1332 | 0·1328 | 0·2550 | 0·2542 |
| IX | 0 2660 | 0·2654 | 0·1320 | 0 1333 |

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# A STUDY OF THE PERIODATES OF ZIRCONIUM

BY R. K. BAHL, SURJIT SINGH AND NARINDER K. BALI

$3ZrO_2, I_2O_7, 14H_2O$ and $4ZrO_2, I_2O_7, 18H_2O$ were formed by the action of disodium paraperiodate and potassium metaperiodate on zirconium nitrate respectively. $6ZrO_2, I_2O_7, 20H_2O$ was formed by the action of paraperiodic acid on freshly prepared zirconium hydroxide. On dehydrating this salt, the lower hydrates were formed whose presence was confirmed by a study of their vapour pressures.

No periodates of zirconium were reported in the literature until recently when Roy Chowdhary (*J. Indian Chem. Soc.*, 1941, **18**, 335) prepared zirconium periodate of the formula $3\,ZrO_2, I_2O_7, 17H_2O$ by the action of disodium paraperiodate on zirconium hydroxide in nitric acid solution. He has not found the available oxygen in the compound.

In the present work the periodates of zirconium have been prepared by the action of disodium paraperiodate and potassium metaperiodate on zirconium nitrate, which yielded zirconium diorthoperiodate, $3ZrO_2, I_2O_7, 14H_2O$ and $4ZrO_2, I_2O_7, 18H_2O$ respectively. Another periodate of zirconium corresponding to the formula $6ZrO_2, I_2O_7, 20H_2O$, has been obtained by the interaction of paraperiodic acid and freshly prepared zirconium hydroxide.

Disodium paraperiodate and paraperiodic acid used were prepared by Wells' method (*Amer. Chem. J.*, 1901, **26**, 278) as modified by Partington and Bahl (*J. Chem. Soc.*, 1934, 1086). Potassium metaperiodate was prepared by the action of chlorine on a boiling solution of potassium hydroxide in presence of iodine (*cf.* Bahl and Singh, *J. Indian Chem. Soc.*, 1940, **17**, 167).

The analysis of the periodates of zirconium was carried out as follows. The zirconium was stimated by changing a weighed amount of the periodate to the corresponding sulphate by heating it with strong sulphuric acid and then igniting it to a constant weight of zirconium dioxide, $ZrO_2$. The available oxygen in the sample was determined by the method adopted by Partington and Bahl (*loc. cit.*). The iodine was estimated by Kimmin's method as modified by Partington and Bahl (*loc. cit.*).

## EXPERIMENTAL

### *Preparation of Salts*

(*a*) A suspension of disodium paraperiodate in water was added gradually to an aqueous solution of excess of zirconium nitrate at room temperature with a continuous stirring. A thick white precipitate was formed immediately. (*b*) A bulky white precipitate was obtained by the addition of a hot solution of potassium metaperiodate to a strong solution of zirconium nitrate. (*c*) An excess of a dilute solution of paraperiodic acid was added, gradually with constant stirring to a thin suspension of zirconium hydroxide, freshly prepared by the action of ammonium hydroxide on a solution of zirconium nitrate and then washing it free of the soluble salts.

The precipitate obtained in each case was filtered, washed and dried at 45° in an electric air oven. The dry salts were in the form of white powders, which looked crystalline under the microscope. These were analysed for zirconium, iodine and available oxygen (Table I).

TABLE I

| | Salt (*a*). | | | Salt (*b*). | | | Salt (*c*). | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample. | Zr. | $I_2$. | Available $O_2$ | Zr. | $I_2$ | Available $O_2$. | Zr. | $I_2$. | Available $O_2$. |
| 1 | 28·32% | 25·46% | 11·05% | 30·79% | 21·20% | 9·35% | 37·29% | 17·91% | 7·58% |
| 2 | 28·33 | 25·24 | 10·62 | 31·16 | 21·67 | 9·29 | 37·69 | 17·31 | 7·50 |
| 3 | 28·38 | 25·21 | 10·95 | 31·01 | 21·53 | 9·48 | 37·36 | 17·72 | 7·68 |

The values for salt (*a*) agree with the formula $3\ ZrO_2, I_2O_7, 14H_2O$. The calculated values for zirconium and iodine are 27·70 and 25·71% respectively. The available oxygen according to the decomposition:

$$3ZrO_2, I_2O_7, 14H_2O = 3ZrO_2 + I_2 + 3\tfrac{1}{2}O_2 + 14H_2O \text{ is } 11{\cdot}34\%$$

The values for salt (*b*) correspond with the formula $4ZrO_2, I_2O_7, 18H_2O$; the calculated values being Zr, 30·67%; $I_2$, 21·47% and the available oxygen according to the equation

$$4ZrO_2, I_2O_7, 18H_2O = 4ZrO_2 + I_2 + 3\tfrac{1}{2}O_2 + 18H_2O \text{ is } 9{\cdot}46\%$$

The calculated values for the formula $6ZrO_2, I_2O_7, 20H_2O$ being Zr, 37·60%, I, 17·33%, and available oxygen according to the equation [*cf.* salt (*c*)]

$$6ZrO_2, I_2O_7, 20H_2O = 6ZrO_2 + I_2 + 3\tfrac{1}{2}O_2 + 20H_2O \text{ is } 7{\cdot}69\%$$

### *Effect of Heat on Zirconium Periodate*

Zirconium periodate, $6ZrO_2, I_2O_7, 20H_2O$ was taken in an uncovered weighing bottle and heated in an electric hot air oven with no loss of weight upto 60°. Above this temperature the dehydration was appreciable in the beginning but was very slow towards the end even at 100°. The different hydrates formed at the various temperatures are given below:

TABLE II

| Temp. | Periodate hydrate | Temp | Periodate hydrate. |
|---|---|---|---|
| 45° | $6ZrO_2, I_2O_7, 20H_2O$ | 81° | $6ZrO_2, I_2O_7, 6H_2O$ |
| 60° | $6ZrO_2, I_2O_7, 13H_3O$ | 98° | $6ZrO_2, I_2O_7, 4H_2O$ |
| 70° | $6ZrO_2, I_2O_7, 8H_2O$ | 120° | $6ZrO_2, I_2O_7$. |

A study of their vapour pressures confirms the existence of all the above hydrates.

The salt was placed in a small tube connected to a vacuum pump and a manometer, which rendered a high vacuum at the room temperature. The stop-cock connecting the pump was then closed, so that only the manometer and the tube were left connected. The tube was heated in a water-bath at a constant temperature of 98°. The vapour pressures of the different hydrates as well as of the mixtures of different hydrates are given in Table III.

TABLE III

| | Hydrated salt. | Vapour pressure. | Mixture of | Vapour pressure. |
|---|---|---|---|---|
| A. | $6ZrO_2, I_2O_7, 20H_2O$ | 5·0 mm. | E+D | 2·5 mm. |
| B. | $6ZrO_2, I_2O_7, 13H_2O$ | 4·5 | E+D+C | 3·5 |
| C. | $6ZrO_2, I_2O_7, 8H_2O$ | 3 5 | E+D+C+B | 4·5 |
| D. | $6ZrO_2, I_2O_7, 6H_2O$ | 2 5 | E+D+C+B+A | 5·0 |
| E. | $6ZrO_2, I_2O_7, 4H_2O$ | 1 5 | | |

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# THE QUESTION OF ACTIVATED OXALIC ACID

By P. S. MacMahon and B. B. Lal

The active agent immediately responsible for the reduction of $HgCl_2$ by permanganate treated oxalic acid appears to be the unstable acid $HMn(C_2O_4)_2$. The latter decomposes spontaneously producing $CO_2'$-ions :

$$Mn(C_2O_4)'_2 \longrightarrow MnC_2O_4 + CO_2 + CO_2'$$

In the presence of free oxalic acid only, the reducing activity ceases immediately upon the disappearance of $HMn(C_2O_4)_2$. There is no evidence of any activated form of oxalic acid persisting in aqueous solution. Mixtures of $KMnO_4$ and anhydrous oxalic acid do not reduce mercuric chloride in acetone. Neutral $K_2C_2O_4$ slowly decolourises $KMnO_4$ at concentrations of the latter below $10^{-5}N$ leaving optically clear solutions. The latter under nitrogen retain the power of reducing $HgCl_2$ for periods up to 24 hours at room temperature in the dark The retention of activity is due to the formation of stable $K_3Mn(C_2O_4)_3$ under these conditions. $KMnO_4$ added to neutral oxalate in concentrations between $10^{-5}$ and $10^{-5}N$ shows a direct relationship between the amount added and the yield of calomel.

The half-ion $CO_2'$ (or $C_2O_4''$) initiates a chain mechanism They are straight chains of great length not involving regeneration of tervalent manganese as part of the mechanism The formation of $H_2O_2$ and the slow catalytic oxidation of oxalic acid in the presence of $Mn^{II}$ are complicated reactions not necessarily involving the assumption of an activated form of oxalic acid. The inhibitory action of oxygen affects the chain process and not any of the permanganate reduction products initiating the reaction. Traces of $Mn^{II}$ ions retard the iodine-oxalate reaction both in air and under nitrogen using oxalate concentrations over $N/10$ There is no evidence of any action of atmospheric oxygen on $CO_2'$-ions producing a peroxide of carbon

In a previous communication (*J. Indian Chem. Soc.*, 1940, **17**, 429) we drew attention to the possibility of correlating the mechanism of the after-effect in the oxalate-iodine reaction with the so-called activation of oxalic acid brought about by the addition of small quantities of oxidising agents such as potassium permanganate in aqueous solution.

We came to the conclusion, however, that the mechanism of these two reactions is quite distinct, since end solutions in the iodine-oxalate reactions, when all the iodine had been used up photochemically, were not found to have the reducing effect on mercuric chloride characteristic of permanganate treated oxalate. This conclusion was based on the assumed existence of an "activated" form of oxalic acid of abnormally long life surviving at the end of the latter reaction. It may be stated at once that we now find no evidence for the existence of such an activated form, so that the possibility of similar reaction mechanisms can no longer be excluded.

Attention to the permanganate-oxalic acid reaction was first drawn by Dhar (*J. Chem. Soc.*, 1917, **111**, 690) who regarded it as an example of induced oxidation. The idea of the formation of a more active energy-richer form of oxalic acid appears to have originated with Oberhauser and Hensinger (*Ber.*, 1928, **61**, 521) who thought they had obtained experimental evidence of its persistence in solution for long periods (up to 24 hours at room temperature) after the permanganate had been used up in the presence of a large excess of oxalic acid. This evidence consisted mainly of the fact that hydrogen peroxide is formed when such solutions continue to be exposed to air or oxygen. The activated oxalic acid could react equally well with mercuric chloride or oxygen, or any other suitable acceptor :

$$2HgCl_2 + H_2C_2O_4^* \longrightarrow 2CO_2 + 2HgCl + 2HCl$$
$$O_2 + H_2C_2O_4^* \longrightarrow 2CO_2 + H_2O_2$$

The above conclusions were shown to be erroneous by Wieland and Zilg (*Annalen*, 1937, **530**, 257) who obtained the same quantities of hydrogen peroxide by bubbling oxygen through solutions containing the same concentrations of oxalic acid to which had been added $Mn^{II}$ ions equivalent in amount to the permanganate used in previous experiments.

Oberhauser and Schormüller (*ibid.*, 1929, **470**, 111) furthermore stated that an aqueous medium was not necessary for the activation. They claimed to have obtained the activated acid using acetone as solvent.

We have carefully repeated this work in a number of experiments using the method mentioned later, and have been wholly unable to confirm their results.

Acetone was purified by distillation over solid potassium permanganate and redistilled over calcium chloride. Acetone solutions of pure anhydrous oxalic acid and of mercuric chloride were mixed and freed from oxygen by passing nitrogen slowly through the mixture for some hours and the acetone solution of potassium permanganate added in the sealed vessel in the dark. A slight brownish precipitate was obtained which turned white overnight. Analysis proved it to be manganese oxalate, $MnC_2O_4$, and there was no trace of calomel. No reduction was obtained by varying the order in which the reactants were mixed. Furthermore, we have been unable to confirm the statement of Oberhauser and Schormüller (*loc. cit.*) that after removal of all the manganese by the usual analytical means, the existence of the activated form of oxalic acid could still be established in the filtrate. In these particular experiments, using potassium permanganate as inductor, we have never been able to observe the reduction of mercuric chloride unless manganese is present in some form or other.

Oberhauser subsequently abandoned the idea of the existence of oxalic acid in two tautomeric forms, one more reactive than the other, and suggested that the activated form is a labile intermediate state between the normal homopolar molecule and complete ionisation, containing excited electron-pairs forming the hydrogen-oxygen linkages.

Wieland and Zilg (*loc. cit.*) were able to disprove the assertion that an active form of oxalic acid was stable over long periods, by performing the experiments under nitrogen. Mercuric chloride was added to permanganate-treated oxalic acid at definite intervals after decolourisation. The latter was found to have almost completely lost its activity after two minutes. These authors have considered that the activation of the oxalic acid molecule is brought about by absorption of energy derived from the primary oxidation process; the hydrogen linkage is "loosened" and so the hydrogen reacts more readily with a suitable acceptor and the acid residue conveys part of the liberated energy to further oxalic acid molecules, thereby initiating a kind of energy chain in solution.

In the course of this investigation we noticed that by adding small quantities of potassium permanganate to *neutral* potassium oxalate solution, the colour gradually disappeared without the visible appearance of manganese dioxide below certain limits of concentration of the former, and the clear colourless solution so obtained strongly reduced mercuric chloride in the dark under nitrogen. Examination in the ultra-microscope failed to reveal colloidal particles of hydrated manganese dioxide. In the following experiments the concentration of potassium permanganate in the reacting solution was usually at a maximum of about $4 \times 10^{-3}N$. When larger quantities of potassium permanganate are employed, the brown colour of hydrated manganese dioxide makes its appearance. If the reaction consists in the oxidation of free oxalic acid derived from the slight hydrolysis of potassium oxalate, there should be a slight appearance of alkalinity, resulting in the formation of $Mn(OH)_2$ above a certain small limiting concentration of permanganate. It is noteworthy that Fox, Swinehart and Garrett (*J. Amer. Chem. Soc.*, 1941, **63**, 1779) have determined the solubility of the latter to be $0{\cdot}4 \times 10^{-6}$ moles per litre, which is of the same order as the concentration of potassium permanganate used in these experiments.

In all experiments conductivity water was used and there was no loss of potassium permanganate over many months, showing the absence of organic reducing impurities.

The reactions using neutral oxalate in place of the free acid, in common with the latter, are inhibited by atmospheric oxygen. After admixture with mercuric chloride, it becomes susceptible to light (*Eder reaction*) so that all experiments had to be carried out rigorously in the dark and under nitrogen.

## EXPERIMENTAL

The experiments were carried out in pyrex glass flasks fitted with a sealed-on bulb containing the requisite quantity of mercuric chloride and another side-tube containing either potassium permanganate solution, solid potassium permanganate, or $MnO_2$. Nitrogen was bubbled for some hours through the oxalate solution and the whole sealed off. Manganese was then added and subsequently mercuric chloride at stated intervals. The mixtures were found to be highly susceptible to traces of alkali from soda glass. When the solutions of potassium oxalate underwent a preliminary boiling in a current of nitrogen to expel air and the usual procedure followed after cooling, they reacted immediately on admixture with mercuric chloride in the dark. No reactivity was found in blank experiments using pyrex vessels, taking care not to give too much preliminary heating. The following experiments represent some of the results obtained, using both the free acid and neutral potassium oxalate.

### *Reaction between "Activated" Free Oxalic Acid and Mercuric Chloride*

The reacting solutions were in all cases brought up to 50 c.c. at room temperature. At the end of the times stated, the flasks were cut open and the mercurous chloride filtered off, dried and weighed.

*Expt.* 1.—*N*-$H_2C_2O_4$(25 c.c.) was treated with solid $KMnO_4$ (0·01 g.). When all the purple colour had disappeared and only a yellowish brown solution remained, 20 c.c. of 5% mercuric chloride solution were added. There was a quantitative reduction in 3 hours. The above experiment was repeated. When the yellowish brown solution had been obtained, air was admitted and mercuric chloride then added. The reduction to calomel was now very largely diminished, although the brown colour took longer to disappear.

*Expt.* 2.—About 0·01 g. of solid potassium permanganate was added to 20 c.c. of *N*-$H_2C_2O_4$ and $HgCl_2$ added as soon as possible after the yellowish brown colour was no longer visible. No reduction whatever to mercurous chloride took place even after standing 24 hours in the dark. The estimated interval after decolourisation was 1 to 2 minutes.

These experiments confirm the results of Wieland and Zilg (*loc. cit.*) and show that there is no justification for assuming the continued existence of an activated form of oxalic acid after the inductor is used up. So long as these solutions were visibly coloured brown and mercuric chloride added there was quantitative reduction, but with the means at our disposal it was impossible to say at what precise instant the brown substance disappeared. This substance is unstable and disappears spontaneously at room temperature within a few minutes. On warming the sealed flask gently the solution suddenly becomes colourless and is suffused with minute bubbles of $CO_2$. It is thus a higher unstable compound, probably of tervalent manganese and will be discussed later. With potassium oxalate it forms the pink complex salt $K_3Mn(C_2O_4)_3$. This was easily shown by adding excess of potassium oxalate to the brown solution from a side-bulb, when the pink colour immediately appeared. In our experiments the latter remained for 24 hours in the dark and reduced mercuric chloride quantitatively. It decolourises immediately in sunlight and is undoubtedly $K_3Mn(C_2O_4)_3$. The stability is greater, the greater the excess of acidified potassium oxalate.

It thus appears from these experiments that the primary oxidation of oxalic acid by potassium permanganate is not an essential part of the process of "activation".

It has sometimes been stated that the reactant immediately responsible is the complex salt. That this is not the case can be shown by substituting solid hydrated $MnO_2$ for potassium permanganate. The former was prepared by the electrolysis of $MnSO_4$ solution, as the specimens prepared by the usual methods of reducing potassium permanganate were invariably found to contain potassium. On adding small fragments of about 0·01 g. of hydrated $MnO_2$ from a side-tube the same brown coloured solution was obtained, with the same reducing effect on mercuric chloride.

It may be mentioned that a highly reactive pink substance may be obtained by treating pure concentrated oxalic acid with the solid $MnO_2$ hydrate. A vigorous reaction takes place with evolution of heat and $CO_2$. If filtered rapidly a red solution is obtained stable for some time in the presence of excess concentrated oxalic acid. On dilution it gives a brown substance containing much hydrogen peroxide, which becomes colourless with further evolution of $CO_2$. The pink solution readily reduces mercuric chloride in air and appears to be either a *peroxalate* of manganese, or free mangani-oxalic acid $H_3Mn(C_2O_4)_3$.

In all the above experiments, substitution of $Mn^{II}$ ions for $KMnO_4$ gave negative results with mercuric chloride under nitrogen. We have thus reason to believe that the reaction is initiated, not by the energy liberated in the primary oxidation (dehydrogenation) of oxalic acid, but by $Mn^{III}$ ions or some complex capable of producing them. An overall equation at the manganic stage may be written as

$$MnO_4' + 5C_2O_4'' + 8H^+ \longrightarrow Mn(C_2O_4)_3''' + 4CO_2 + 4H_2O.$$

As previously stated, experiments were carried out using neutral solutions of potassium oxalate to which small quantities of $KMnO_4$ had been added up to a limit not exceeding $10^{-5}N$. The pink colour of the permanganate took some time to disappear at room temperature leaving an optically clear solution.

TABLE I

| $HgCl_2$ added after addition of $KMnO_4$ at intervals of | Mercurous chloride formed | | |
|---|---|---|---|
| | Expt. 3. at 26°. | Expt. 4 at 26°. | Expt 5 at 34°. |
| 0 hour | *0·7564 g. | *0·8678 g. | *0·8856 g |
| 1 | 0·3032 | 0·8712 | 0·8774 |
| 2 | 0·1968 | 0·5478 | 0·6582 |
| 3 | — | — | 0·3046 |
| 4 | 0·0062 | 0·3432 | — |
| 6 | — | — | 0·0748 |
| 8 | — | 0·0132 | — |
| 12 | 0·0036 | 0·0050 | 0·0048 |
| 16 | 0·0028 | 0·0032 | — |
| 24 | A faint opalescence | Opalescence | Opalescence |

* Simultaneous addition of $KMnO_4$ and $HgCl_2$ to potassium oxalate.

*Reaction between* $K_2C_2O_4$, $KMnO_4$ *and* $HgCl_2$

*Expt.* 3.—$N$-$K_2C_2O_4$ (25 c.c.), 5% $HgCl_2$ (20 c.c.), $N/209$-$KMnO_4$ (0·4 c.c.) and water (4·6 c.c.) were taken and the reaction allowed to proceed for 1 hour at 26°. Nitrogen was passed through oxalate solution, and after the vessel had been sealed off, $KMnO_4$ was added from a side-bulb. $HgCl_2$ was then added at various intervals after the addition of $KMnO_4$ as shown in Table I. The mixture was kept in the dark for 1 hour and $Hg_2Cl_2$ filtered off and weighed.

*Expt.* 4.—Expt. 3 was repeated under the same conditions, but the reaction was allowed to proceed for 24 hours at 26° (Table I).

When the above experiments were repeated in presence of air, there was practically no reduction even after 24 hours' standing in the dark.

*Expt.* 5.—Experiment 4 was repeated using further recrystallised reagents. Temperature of the experiment was 34° (Table I). This result has been shown in Fig. 1.

*Expt.* 6.—$N$-$K_2C_2O_4$ (25 c.c.), 5% $HgCl_2$ (20 c.c.) and water (4 6 c.c.) were mixed together under nitrogen with varying amounts of potassium permanganate and the reaction allowed to proceed for 24 hours at 34° (see Fig. 2).

TABLE II

| | | | | |
|---|---|---|---|---|
| Conc. of $KMnO_4$ ($N$) ... | $4 \times 10^{-5}$ | $4 \times 10^{-6}$ | $4 \times 10^{-7}$ | $4 \times 10^{-8}$ |
| $Hg_2Cl_2$ (g.) .. | 0·8674 | 0·6594 | 0·2718 | 0·0136 |

These experiments show that at the higher concentrations of $KMnO_4$ employed the reaction takes many hours to complete in spite of the fact that some free oxalic acid must be liberated by the addition of $HgCl_2$ solution. When the permanganate has partly disappeared after some hours and is thus present in very low concentrations on addition of mercuric chloride, a comparison of Table I (Expt. 3 and 4) shows that the reaction has now been completed within 1 hour. No further increase in weight of precipitated calomel took place after one week in the dark. Blank experiments, taking the precautions already mentioned, showed no reaction between potassium oxalate and mercuric chloride.

The extent of the reactions in Expt. 5 is shown in Fig. 1. The course is continuous from the highest concentration of $KMnO_4$ employed down to the vanishingly small concentrations, colourless to the eye. In Expt. 6 the permanganate solutions added at the lower concentrations were quite colourless. Fig. 2 shows that there is a direct proportionality between the amount of $KMnO_4$ added and the amount of $HgCl_2$ reduced.

FIG. 1

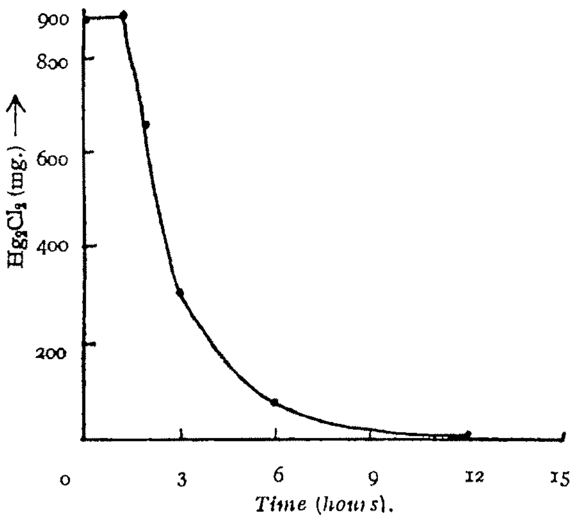
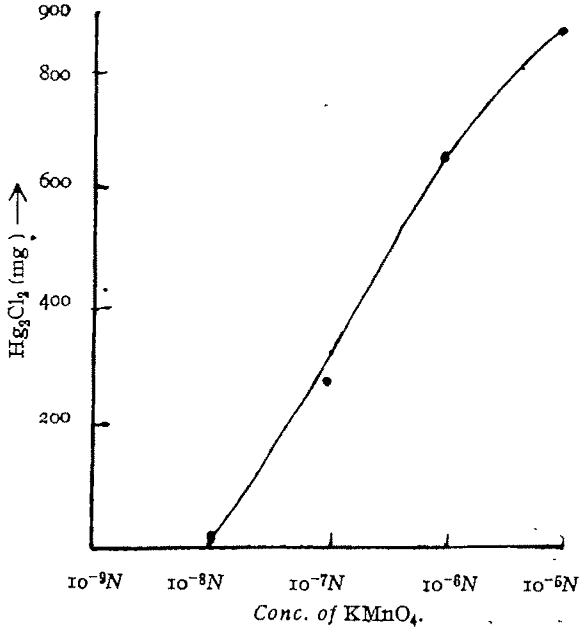


FIG. 2



When potassium permanganate is reduced by acidified oxalate solution, a series of colour changes takes place before complete decolourisation corresponding to successive reduction of the $MnO_4'$ ion to colourless $Mn^{II}$ ion.

The foregoing experiments using oxalic acid and either $KMnO_4$ or $MnO_2$ as oxidising agent show that the active agent, which brings about reduction, is the brown substance appearing for a short time immediately prior to decolourisation. This alone disposes of Wieland's theory that the reaction depends upon the energy liberated in the primary oxidation of oxalic acid molecules by potassium permanganate Even when pure oxalic acid and solid $MnO_2$ are used the same brown solution makes its appearance so that the reaction only goes partly at least in the direction :—

$$MnO_2 + 2H_2C_2O_4 \longrightarrow 2H_2O + MnC_2O_4 + 2CO_2$$

or

$$MnO_2 + H_2C_2O_4 \longrightarrow H_2O_2 + MnC_2O_4$$

(Manganese dioxide is a complex substance, the formula of which might be more appropriately written $MnO{\cdot}MnO_3$ or $3\,MnO{\cdot}Mn_2O_7$. *cf.*, Spring and Lucion, *Bull. Soc. chim.*, 1890, *iii*, **3**, 4)

There is reason to believe that the active brown substance is derived from mangani-oxalic acid as follows :—

$$(i)\quad \underset{\text{(Cherry red).}}{Mn(C_2O_4)_3'''} \longrightarrow C_2O_4'' + \underset{\text{(Brown).}}{Mn(C_2O_4)_2'}$$

$$(ii)\quad Mn(C_2O_4)_2' \longrightarrow MnC_2O_4 + CO_2 + CO_2'$$

Previous workers on the Eder reaction have shown that it possesses a chain mechanism with a high quantum yield (Roseveare, *J. Amer. Chem. Soc.*, 1930, **52**, 2619) and the nature of the dark chemically induced reaction also points to a chain mechanism. The chains must originate from active $CO_2'$ (or $C_2O_4''$)* ions produced as above (*ii*); the same ion has been postulated as one of the chain carriers in the iodine-oxalate reaction and its accompanying after-effect (*J. Indian Chem. Soc.*, 1940, **17**, 429). Launer (*J. Amer. Chem. Soc.*, 1932, **54**, 2597 *et seq.*), who has already proposed a mechanism depending upon the presence of this ion, claims to have identified the ion $Mn(C_2O_4)_2'$ present as follows :—

$$Mn^{+++} + 2C_2O_4'' \rightleftharpoons \underset{\text{(Cherry red)}}{Mn(C_2O_4)_2'}$$

We prefer to think, however, that the cherry red colour is due to the complex potassium salt formed as already described.

According to Launer (*loc. cit.*) an aqueous solution of $KMnO_4$ always contains in equilibrium $MnO_4'$, $Mn^{IV}$, $Mn^{III}$ and $Mn^{II}$ ions.

$$(iii)\quad 2MnO_4' + 3Mn^{++} + 16H^+ \rightleftharpoons 5Mn^{++++} + 8H_2O \text{ (rapid equilibrium,}$$

$$(iv)\quad Mn^{++++} + Mn^{++} \rightleftharpoons 2Mn^{+++}$$

There is little or no reaction between $MnO_4'$ and $C_2O_4''$ in the absence of $Mn^{++}$. The reactions which take place are as follows :—

$$(v)\quad Mn^{++++} + C_2O_4'' \longrightarrow Mn^{+++} + CO_2 + CO_2' \text{ (measurable)}$$

$$(vi)\quad Mn^{+++} + CO_2' \longrightarrow CO_2 + Mn^{++} \text{ (rapid)}$$

$$(vii)\quad Mn^{+++} + C_2O_4'' \longrightarrow Mn^{++} + CO_2 + CO_2' \text{ (measurable)}$$

$$(viii)\quad Mn^{+++} + CO_2' \longrightarrow Mn^{++} + CO_2 \text{ (rapid)}$$

Applying this scheme to the foregoing experiments with neutral oxalate it is evident that reactions (*v*) and (*vii*) must be instantaneous on account of the large excess of $C_2O_4''$ ions present and

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* In discussing these reactions the active ion may be written either as $CO_2'$ or $C_2O_4''$, since there is no possibility of distinguishing between them.

(*vi*) and (*viii*) must be negligible. Since $KMnO_4$ disappears very slowly, the rapid equilibrium in (*iii*) cannot thus be a governing factor in our experiments.

We suggest that the primary reaction takes place between $KMnO_4$ and free oxalic acid derived from slight hydrolysis of $K_2C_2O_4$, that mangani-oxalic acid is formed as a product of the reduction and that it is instantly stabilised in the presence of excess of $K_2C_2O_4$ as $K_3Mn(C_2O_4)_3$. The equilibrium

$$H_3Mn(C_2O_4)_3 + 2K_2C_2O_4 \rightleftharpoons K_3Mn(C_2O_4)_3 + KH_3(C_2O_4)_2.$$

moves to the right.

Experiments of the type 3 and 6 reveal two principal characteristics, *viz.*, (*a*) the retention by the $KMnO_4$-$K_2C_2O_4$ mixture of its reducing power on $HgCl_2$ for periods up to 24 hours at room temperature and (*b*) the reaction with mercuric chloride takes several hours to complete at the maximum concentration of $KMnO_4$ taken.

The slowness of (*a*) must be due to the slow breaking down of $Mn(C_2O_4)_3'''$ ions, which under the conditions of the experiments will be present in only slight concentration. The $CO_2'$ ions produced will be largely removed by self-combination in the absence of a suitable reactant $CO_2' + CO'_2 \longrightarrow C_2O_4''$ (MacMahon and Lal, *loc. cit.*).

In this connection it may be stated that the same amount of $KMnO_4$ (0·4 c.c. of $N/209$) added to oxalic acid ($N/10$) produces only about one tenth the amount of reduction obtained with potassium oxalate ($N/10$) after standing 24 hours under nitrogen. In the former case self-combination takes place to a large extent as shown by the instability of $HMn(C_2O_4)_2$.

The first effect of adding mercuric chloride, which has an acid reaction in aqueous solution, is to cause the complete conversion of $KMnO_4$ into $K_3Mn(C_2O_4)_3$ within a few minutes at room temperature. Hydrogen ions also have the effect, as established in other experiments, of further stabilising the latter, probably by suppressing the reaction

$$Mn(C_2O_4)_3''' \longrightarrow C_2O_4'' + Mn(C_2O_4)_2'$$

so that the long periods taken for the reduction of $HgCl_2$ to be completed are thus readily accounted for.

If every $CO_2'$ ion produced at the final stage, $Mn(C_2O_4)_2' \longrightarrow MnC_2O_4 + CO_2 + CO_2'$ starts a chain, the total amount of $Hg_2Cl_2$ precipitated will depend upon the number of chains started and hence upon the actual amount of $K_3Mn(C_2O_4)_3$ present on addition of $HgCl_2$.

Experiment 6 shows that a proportionality actually exists between the amount of $HgCl_2$ reduced and the concentration of $KMnO_4$ (Fig. 2). Since there is no room in this mechanism for regeneration of $Mn^{III}$ ions, the reaction appears to furnish a proof of the occurrence of long straight reaction chains in aqueous solution. It may be noted that experiments performed under these conditions furnish an extremely sensitive test for the presence of $MnO_4'$ ions, down to concentrations of the order $10^{-8}N$.

While this work was in progress, a paper appeared (Cartledge, *J. Amer. Chem. Soc.*, 1941, **63**, 906) proposing the following mechanism for the actual chain process in postulating a second chain carrier $Hg^+$:—

$$\begin{aligned} C_2O_4' + Hg^{++} &\longrightarrow 2CO_2 + Hg^+ \\ Hg^+ + C_2O_4'' &\longrightarrow Hg + C_2O_4' \\ Hg + Hg^{++} &\longrightarrow Hg_2^{++} \text{ (as } Hg_2Cl_2) \end{aligned}$$

### *Formation of Hydrogen Peroxide and Action of Manganous Ions*

The fact that hydrogen peroxide is formed when $KMnO_4$ is decolourised by an excess of oxalic acid has lent support to the conception of an activated form of the latter. The matter is further complicated by the inhibitory effect of oxygen in the reduction of mercuric chloride, Experiments 1 and 4, however, show that the inhibitory effect takes place after the $Mn^{III}$ stage when all the permanganate has disappeared. It is thus *not* due to the competitive dehydrogenation by atmospheric oxygen of oxalic acid activated by the energy liberated in the primary oxidation as postulated by Wieland.

Experiments 1 and 4 repeated in air and in the dark showed only a faint opalescence after 4 days. The same result was observed by substituting $MnSO_4$ equivalent in amount to the permanganate (0·00005 g. $MnSO_4$). There was much $H_2O_2$ present after 6 months.

*Expt.* 7.—When, however, larger quantities of manganese sulphate were employed (0·05 to 0·5 g.) with $K_2C_2O_4$, precipitation of $Hg_2Cl_2$ in bulk began to take place after 48 hours in the dark, gradually increasing in rate, with the appearance of the characteristic colour of $K_3Mn(C_2O_4)_3$. This phenomenon was unaffected by the order in which the reactants were mixed.

A solution of 25 c.c. of *N*- $K_2C_2O_4$ to which 1 g. of $MnSO_4$ had been added showed no pink colour after one week; when, however, three drops of dilute sulphuric acid had been added, it appeared in a few hours in the dark and diffused light. Much hydrogen peroxide was invariably present along with the latter.

It thus appears that in the presence of oxygen and pure oxalic acid $Mn^{II}$ ions are converted into $Mn^{III}$ ions and the latter are stabilised as $K_3Mn(C_2O_4)_3$ in the presence of excess of $C_2O_4''$ ions.

Richardson (*J. Chem. Soc.*, 1894, **65**, 450) has found that oxalic acid itself is oxidised in the presence of oxygen and light, giving $H_2O_2$ if the oxygen is in excess, and $H_2O$ if in defect.

In view of Winther's finding (*Z. wiss. Phot.*, 1909, **7**, 409 ; 1910, **8**, 197 237) that the Eder reaction does not take place when the materials used are completely freed from iron, it might be desirable to repeat Richardson's work with oxalic acid known to be iron-free. According to Winther, 0·047 mg. $FeCl_3$ per litre is sufficient to induce the Eder reaction.

Jorissen and Reicher (*Z. physikal. Chem.*, 1899, **31**, 142) found that $Mn^{II}$ ions catalysed the oxidation of oxalic acid both in light and in the dark, that acids accelerated the oxidation and that the rate increased with the concentration of $Mn^{II}$ ions.

From the foregoing it appears that the formation of hydrogen peroxide is not necessarily connected with the agency of any special form of activated oxalic acid of long life. The matter is decidedly complicated and is probably connected with the still imperfectly understood mechanism of the Eder reaction. Oxalic acid oxidises in the two directions above mentioned under conditions not yet elucidated.

Catalysis of the slow oxidation by $Mn^{II}$ ions might be represented as follows by an overall equation, without theorising about the mechanism, since 95 % of the ionisation of *N*/10-oxalic acid at ordinary temperatures are represented by the first stage:—

$$(i)\quad 2MnC_2O_4 + O_2 + 2HC_2O_4' + 2H^+ \longrightarrow 2HMn(C_2O_4)_2 + H_2O_2$$

$$(ii)\quad Mn(C_2O_4)_2' \longrightarrow MnC_2O_4 + CO_2 + CO_2'$$

$$(iii)\quad 2CO_2' \longrightarrow C_2O_4''$$

The net effect would be to oxidise oxalic acid to hydrogen peroxide leaving the $Mn^{II}$ ions unchanged. In accordance with what has been said previously this would also account for the appearance of the pink colour in presence of excess $K_2C_2O_4$ :—

$$HMn(C_2O_4)_2 + 2K_2C_2O_4 \longrightarrow K_3Mn(C_2O_4)_3 + KHC_2O_4$$

In experiment 7 after about 48 hours in the dark, copious precipitation of calomel takes place along with the appearance of the pink colour and hydrogen peroxide. Under these conditions there is apparently a long induction period and after that oxygen exercises no inhibitory effect. Something similar was found by Winther (*loc. cit.*) in the catalysis of the Eder reaction by iron salts. In the presence of a small amount of iron, oxygen retards the reaction; when the concentration of iron is high, oxygen somewhat increases the photo-rate.

Matters are complicated by high concentration of manganese ions and the number of different reactions taking place simultaneously. It has already been shown that in these mixtures tervalent manganese gradually accumulates. It can only be suggested that there arises a deficiency of oxygen in solution and the eventual high rate of chain initiation overcomes the inhibitory effect. It is to be noted that the pink colour remains stable in solution after the precipitation of calomel has ceased.

### *Oxygen Inhibition*

When fresh hydrogen peroxide is added to the brown solution assumed to contain $HMn(C_2O_4)_2$ the colour is discharged. Furthermore, as noted in Expt. 4 admission of oxygen actually prolongs the life of the brown substance but largely diminishes the yield of $Hg_2Cl_2$. This disposes of the possibility of the inhibitory action of oxygen being traceable to the destruction of the active manganic compound. The immediate effect appears to be rather the regeneration of tervalent manganese.

It is to be inferred, therefore, that the inhibitory effect is due to the removal of one or other of the chain-carriers. The mechanism of the process has not yet been satisfactorily explained.

Roseveare (*J. Amer. Chem. Soc.*, 1933, **55**, 870) has put forward a scheme based upon the formation in air of a permonocarbonic acid, $CO_4'$, which acts as follows:—

$$CO_2' + O_2 \longrightarrow O_2CO_2' \text{ (rapid, reversible)}$$

$$O_2CO_2' + Mn^{++} + 2H^+ \longrightarrow Mn^{+++} + CO_2 + H_2O_2$$

We have endeavoured to test the consequences of this when applied to the iodine-oxalate photo-reaction, in the mechanism of which the participation of $C_2O_4$ has been postulated.

In the first instance, it may be observed that the presence of a highly reactive peroxide of this type should tend to form hydrogen peroxide, liberate fresh iodine from potassium iodide and so produce an apparent retardation of the reaction. We find no different behaviour in the latter, however, when carried out under nitrogen using the method already described.

Further experiments have been tried on the effect of the addition of small quantities of $Mn^{II}$ ions to the reaction mixtures.

To solutions of 25 c.c. of *N*, *N*/4, and *N*/10-$K_2C_2O_4$ were added 0·001 g. of $MnSO_4$ and 1 c.c. of *N*/10-iodine in the dark, the mixtures then exposed to diffused light and the time of iodine decolourisation noted. Retardation of the photo-reaction actually takes place, but it is of the same order under nitrogen as in air. The disappearance of iodine is accompanied by the appearance of the characteristic pink colour of $K_3Mn(C_2O_4)_3$ in all cases, which remains for long periods even in the presence of diffused light if a few drops of dilute sulphuric acid have been previously added. Here the iodine evidently acts as a transport catalyst. So far as these experiments are concerned, there is thus no evidence for the existence of a peroxide of carbon in the presence of oxygen. The retardation may be simply due to the reaction

$$Mn^{++} + I \longrightarrow Mn^{+++} + I'$$

It is possible that oxygen may affect the other chain-carrier, $Hg^+$, postulated by Roseveare, but this for the present must remain a matter of conjecture.

Failure to obtain reduction by adding $HgCl_2$ to the end solutions in the iodine-oxalate reaction may be accounted for by the fact that *two* chains depending upon the maintenance of a small stationary concentration of a common carrier would now have to be operative, namely, the Berthoud chain in the latter and the Cartledge chain. Conditions are thus present for a bifurcation of the energy-channels, which takes place apparently at the expense of the reaction

$$C_2O_4' + Hg^{++} \longrightarrow 2CO_2 + Hg^+$$

Finally it may be stated that experiments now in progress show that none of the other simple carboxylic acids reduces mercuric chloride in the presence of potassium permanganate at room temperature in a manner comparable with that of oxalic acid; the unique character of the latter in this respect appears to be due to the reactive half-ion.

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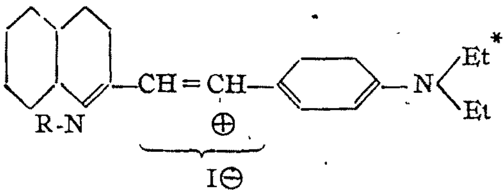
# PHOTOGRAPHIC SENSITISERS DERIVED FROM QUINALDINE

By M. Q. Doja and Dhanushdhar Prasad

In an attempt to prepare a photographic sensitiser suitable for use in the manufacture of panchromatic plates, a set of new sensitisers has been prepared by the condensation of *p*-diethylaminobenzaldehyde with quinaldine-methiodide, -ethiodide, -*n*-propyl iodide and -*n*-butyl iodide, in presence of piperidine as a catalyst. The dying, optical, photographic and other properties of these dyestuffs have been examined. The preparation and properties of quinaldine-*n*-propyl iodide and quinaldine-*n*-butyl iodide have been described for the first time. The future line of research for the synthesis of the proposed sensitiser has also been discussed.

In a previous communication (Doja and Prasad, *J. Indian Chem. Soc.*, 1942, **19**, 377) it has been reported that the attempt to prepare a photographic sensitiser, which will sensitise uniformly, *without any gap*, from the blue to the red end of the spectrum, and will thus be useful in the manufacture of "panchromatic" plates, was only partly successful. The increase in the molecular weight of the dye did produce, as expected, a shift of the band of extra-sensitisation towards the red, but this was not large enough to make the compound commercially valuable. A further increase in the molecular weight of the dystuff has now been effected, by using quinolinium compounds in place of pyridinium compounds, in the condensation with *p*-diethylaminobenzaldehyde. These syntheses have given rise to a new set of sensitisers, represented by the general formula (J).



[where R=Me, Et, *n*—Pr, *n*—Bu]

(J)

Like other members of the cyanine dye group these compounds are soluble in ionising solvents like water, alcohol and acetic acid, and insoluble in non-ionising solvents like ether, benzene, and chloroform. The solubility in water decreases with increasing molecular weight, the butyl iodide of the dye being nearly insoluble in this liquid. All aqueous solutions are ruby-red, and all alcoholic solutions are magenta in colour, except that of the butyl iodide, which gives a brownish yellow solution exhibiting a weak green flourescence. This solution too turns magenta on dilution with water. The relative intensity of the alcoholic solutions (1 : 50,000) of the methiodide, ethiodide, and *n*-propyl iodide of the dyes, as determined by a Duboscq colorimeter, is given in Table I. It

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[*] In this structure, the iodine (anion) is not attached definitely to either of the two nitrogen atoms. This is due to the fact that in a cyanine dye there is much evidence for supposing that the acidic radical of the dye is not associated with one nitrogen atom more than the other (Mills and Braunholtz, *J. Chem. Soc*, 1922, **121**, 1489; Hamer, *ibid.*, 1928, **127**, 206; also see *J. Soc. Chem.*, *Ind.*, 1922, **41**, 804A; 1935, **54**, 640). Otherwise expressed the positive charge of the dye is shared between the two nitrogens. There exists in fact a kind of resonance within the molecule, in which, the positive charge changes position. The actual constitution of the cation is that of a resonance hybrid of these two structures. It has been suggested that the intense colour and some other properties of the cyanine dyes are due to their resonating structures,

is noteworthy that the ethiodide (L) again (*cf*. Doja and Prasad. *J. Indian. Chem. Soc.*, 1942, **19**, 126; 377) forms the most intensely coloured solution in the series.

TABLE I

| | Depth of the solution of | | | | |
|---|---|---|---|---|---|
| | (K) | (L) | | (M) | |
| | 12 | 10·05<br>10·00<br>10·00 | 10·02 | 16·15<br>16·20<br>16·20 | 16·18 |
| | 7 | 6·40<br>6·40<br>6·40 | 6·40 | 9·00<br>9·05<br>9·05 | 9·03 |
| Relative Intensity. | 1 | 1·19<br>1·09 | 1·14 | 0·74<br>0·77 | 0·75 |

TABLE II

| Compound | Vol. of N/100-HCl required for complete decolourisation of 2 c.c. of Alcoholic soln. (c.c) | | Aq. soln. (c.c.) | |
|---|---|---|---|---|
| (K) | 6·9<br>7·1 | 7·00 | 3·3<br>3·3 | 3·30 |
| (L) | 7·9<br>7·9 | 7·90 | 6·7<br>6·8 | 6·75 |
| (M) | 7·9<br>8·0 | 7·95 | 13·1<br>13·2 | 13·15 |
| (N) | 9·5<br>9·4 | 9·45 | 21·6<br>21·6 | 21·60 |

In Tables I-VI, (K), (L), (M), (N) refer respectively to the methiodide,-ethiodide, *n*-propyl iodide and *n*-butyl iodide of the dye.

The observation of Mills and Pope (*Phot. J.* 1920, **44**, 255) that alcoholic solutions of certain cyanine dyes are more resistant to decolourisation by mineral acids than their aqueous solutions, has been found to be only partly correct with this set of dyes. The solutions of the methiodide and the ethiodide do behave in this fashion, but in the case of the propyl and the butyl iodides, it is the other way round, the aqueous solution being more resistant to decolourisation than the alcoholic solution. It will be seen from Table II that there is a gradual increase in the amount of acid required for complete decolourisation as we ascend the series, this increase being much more pronounced in the case of the aqueous solutions than in the alcoholic.

Except the methiodide, the crystals are all pleochroic, and exhibit characteristic reflexes. Their melting points do not show any regularity. It is, however, interesting to note that the heaviest number of the series, the butyl iodide (N), has the lowest melting point. In Table III are recorded, the shapes, melting points, and optical properties of the crystals.

TABLE III

| Compound. | Shape. | M.p | Colour by reflected light | Colour through transmitted light. | Reflex. | Pleochroism. Colour of light in one position of polariser | Colour after rotation through 90° | Remarks. |
|---|---|---|---|---|---|---|---|---|
| (K) | Aggregates of small opaque irregular crystals. | 190° | Dark green. | Nil | Strong, bottle-green | Nil | Nil | Under the microscope the crystals show a green halo with polarised light |
| (L) | Minute felted needles | 230 | Light chocolate | Dull red | Medium, greenish blue | Orange | Scarlet | — |
| (M) | Microscopic needles. | 198 | Olive green | Dark brownish red (in thin crystals only) | Weak, light green | Reddish brown | Opaque | Shows a violet halo under the microscope with polarised light. |
| (N) | "Dogtooth" crystals | 111 | Brownish yellow | Yellowish green | Weak, blue | Yellowish green | Brown | — |

The methiodide (K), ethiodide (L), and -propyl iodide (M) dye silk, wool and cotton varying hades of blue-violet, the blue component of which increases with increasing molecular weight of the dye. The butyl-iodide (N) produces yellow shades only (Table IV). None of these colours s fast either to sunlight or to washing.

TABLE IV

| Compound | Colour produced on Silk. | Wool. | Cotton. | Remarks |
|---|---|---|---|---|
| (K) | Violet. | Reddish violet | Light violet | In the case of 'L', the ethiodide, wool can be dyed any colour from light salmon to deep blue-red by the addition of 1-5% acetic acid to the dye bath. |
| (L) | Blue-violet | Deep reddish violet | Reddish blue | |
| (M) | Deep blue-violet | Reddish blue | Brinjal blue | |
| (N) | Pinkish yellow | Lemon yellow | Bluish yellow | |

The flourescence of weak solutions (1:50,000) of these dyestuffs in 90% alcohol as determined y the previously described method (Doja, *J. Indian Chem. Soc.*, 1940, **17**, 348) is given in Table V.

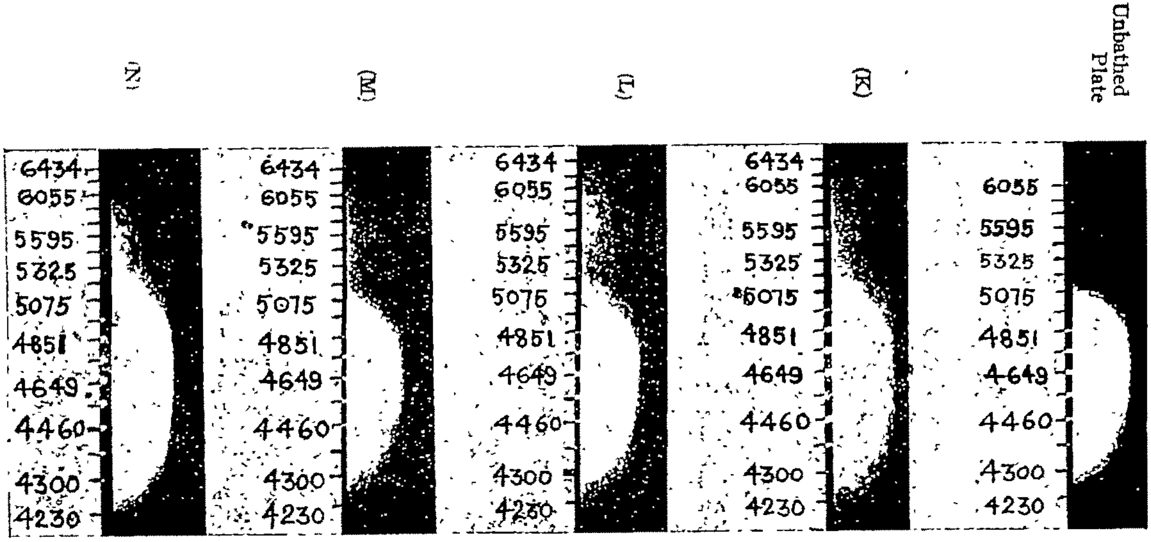
TABLE V

Colour of the flourerscent beam seen at right angles to the incident beam.

| Wallace olour filter No. | (K). | (L). | (M). | (N). |
|---|---|---|---|---|
| 1 | Brilliant red | Red | Dull red | Red |
| 2 | Flaming red | Scarlet | Crimson | Weak red |
| 3 | Light red | Deep pink | Vermilion red | Yellowish green |
| 4 | Weak flaming red | Pink | Rose-red | Flaming red |
| 5 | Red with slight yellow tinge | Orange | Reddish yellow | Yellow |
| 6 | Yellowish red | Weak orange | Orange | Sulphur-yellow |
| 7 | Light absorbed | Light absorbed | Light absorbed | Sky blue |
| 8 | Weak blue (seen with difficulty) | Light arc blue | Weak blue | Grass green |
| 9 | Deep blue | Saphire blue | Blue-violet | Yellowish green |
| 10 | Yellowish red | Orange | Orange | Lemon yellow |

The sensitisation spectra of these compounds are shown in Fig. 1, and the salient features of the spectra have been summarised in Table VI.

FIG. 1.

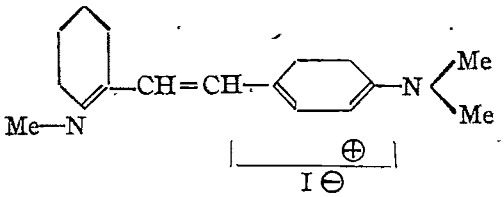


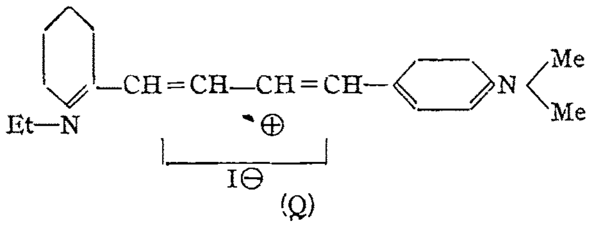
It will be seen that these compounds extend the normal sensitivity of the photographic plate fairly well into the red end of the spectrum, but the bands of extra sensitisation are weak and the "gap" in the blue-green is quite pronounced.

TABLE VI

| Compound | Total range of sensitisation. | Range of uniformly intense sensitisation | Extra sensitisation | |
|---|---|---|---|---|
| | | | Minimum. | Maximum. |
| (K) | 4200-6350 Å | 4400-5250 Å | 5250 Å | 5750 Å |
| (L) | 4200-6400 | 4350 5000 | 5200 | 5800 |
| (M) | 4250-6150 | 4400-5000 | 5200 | 5750 |
| (N) | 4200-6350 | 4350-5000 | 5300 | 5600 |

Comparatively speaking, the -ethiodide of the series is the best sensitiser, extending the sensitisation upto λ6400. It is interesting to note in this connexion, that in the carbocyanine series of dyestuffs too, the -ethiodide is the best photographic sensitiser (Pope and Mills, *Phot. J.*, 1920, **44**, 256). From the point of view, however, of the preparation, of a "*single*" sensitiser, suitable for use in the manufacture of panchromatic plates, these syntheses have not been quite successful. The replacement of pyridine nucleus by quinoline nucleus has reintroduced the chief defect of "red" sensitisers—the failure to sensitise photographic plates for a short region in the blue-green portion of the spectrum. Future attempts, therefore, to increase the size of the original substance, 2-*p*-dimethylaminostyrylpyridine methiodide (P) (Mills and Pope, (*J. Chem. Soc.*, 1922, **121**, 946), with a view to exend its sensitising power farther into the red (Bloch and Hamer, *Phot. J.*, 1930, **70**, 376; Hamer, *J. Chem. Soc.*, 1930, **129**, 995), should not disturb the pyridine molecule, which, in some way seems to be responsible for the valuable "*uniform*" sensitiveness of this compound. Another method of achieving our object, the lengthening of the conjugated chain between the two nitrogen atoms, which is known to shift the bands of extra sensitisation of a cyanine dye towards the red (Bloch and Hamer, *Phot. J.*, 1928, **68**, 24) also does not seem to hold out great hopes, in view of the work of Bloch and Hamer (*Phot. J.*, 1930, **70**, 374), who have prepared *p*-dimethylaminocinnamylidine-α-picoline-ethiodide (Q)


(P)


(Q)

and found it to possess little photographic activity. Under the circumstances, it seems reasonable to suppose, that the only hopeful method of synthesising the desired sensitiser is to increase the size of the radicles attached to either or both of the two nitrogen atoms. Further work in this direction is in progress.

The preparations of quinaldine propyl iodide and quinaldine butyl iodide have been described for the first time. The crystals of these compounds are neither pleochroic nor show any reflex. The propyl iodide was prepared by heating the constituents either in a sealed tube or in an open vessel. The latter method gives a better yield.

## EXPERIMENTAL

*2-p-Diethylaminostyrylquinoline methyl iodide.*—*p*-Diethylaminobenzaldehyde (1·26 g.), quinaldine methiodide (2·03 g.), piperidine (0·5 c.c.) and absolute alcohol (50 c c.) were heated together in a flask under reflux for 5 hours. Within a quarter of an hour beautiful violet crystals appeared. After the solution had cooled, it was slowly concentrated in a vacuum desiccator. The separated crystals were recrystallised from ethyl alcohol, yield 1·26 g. (39·7%). (Found: N, 6·78; I, 28·96. $C_{22}H_{25}N_2I$ requires N, 6·31; I, 28·60 per cent).

2-p-*Diethylaminostyrylquinoline-ethyl iodide.*—*p*-Diethyl-aminobenzaldehyde (2·14 g.), quinaldine ethiodide (3·61 g.) and piperidine (0·5 c.c.) were dissolved in 75 c.c. of absolute alcohol and the solution heated to brisk boiling for 3 hours. On cooling, chocolate coloured crystals were deposited, which were recrystallised from butyl alcohol, yield 4·22 g. (76·3%). (Found: N, 6·34; I, 27·95. $C_{23}H_{27}N_2I$ requires N, 6·11; I, 27·73 per cent).

2-p-*Diethylaminostyrylquinoline-n-propyl iodide.*—*p*-Diethylaminobenzaldehyde (2·4 g.), quinaldine-*n*-propyl iodide (4·2 g), piperidine (0·5 c.c.) and absolute alcohol (35 c.c.) were refluxed together for 7 hours. The mixture was left in a frigidaire overnight and the separated crystals recrystallised from butyl alcohol. A second crop was obtained by concentrating the mother-liquor and recooling it in the frigidaire, total yield 4·0 g. (67%). (Found: N, 6·11; I, 27·08. $C_{24}H_{29}N_2I$ requires N, 5·93; I, 26·91 per cent).

2-p-*Diethylaminostyrylquinoline*-n-*butyl iodide.*—A solution of quinaldine-*n*-butyl iodide (1·1 g.), *p*-diethylaminobenzalddehyde (0·6 g.) and piperidine (0.75 c.c.) in absolute alcohol (30 c.c.) was boiled under reflux for 9 hours. Within half an hour the solution turned scarlet and the colour deepened with the progress of heating. No crystals, however, appeared. The cold solution was slowly evaporated to about half its original volume in a vacuum desiccator and then placed in a frigidaire for 24 hours. The crystals that separated out were recrystallised from butyl alcohol, yield 0·5 g. (31·2%). (Found: N, 5·86; I, 26·25. $C_{25}H_{31}N_2I$ requires N. 5·72; I, 26·13 per cent).

*Quinaldine* n-*propyl iodide*—(Method I).—Quinaldine (8·65 g.; 1 mol.) and *n*-propyl iodide (10·63 g; 1 mol.) were heated together on a water-bath for 30 hours. The mixture was kept in a vacuum desiccator for 48 hours and then cooled in a frigidaire. The brick-red mass, thus produced, was recrystallised from rectified spirit. A second crop of crystals was obtained by the concentration of the mother-liquor, m.p. 145°-46°, total yield 9·73 g. (49·6%). The crystals form rectangular plates, are turmeric in colour and transmit orange-yellow light only. (Found: N, 4·73; I, 41·34. $C_{13}H_{16}NI$ requires N, 4·47; I, 40·58 per cent).

(Method II).—Quinaldine (6·28 g.) and *n* propyl-iodide (6·76 g.) were heated together in a sealed tube for 6 hours at 100°. The red solid after recrystallisation was found to be identical with the product obtained by the first method, yield 4·3 g. (32·9%).

*Quinaldine-*n*-butyl iodide.*—Quinaldine (8·0 g.) and *n*-butyl iodide (10·3 g.) were refluxed together on a steam-bath for 34 hours. The solution was left in a vacuum desiccator for 3 days and then in a frigidaire for 24 hours. The separated solid was filtered off, placed on a porous plate and then recrystallised from 90% alcohol, m.p. 193°, yield 3·5 g. (19·1%). The crystals are originally pink in colour but after a few days gradually turn straw. They crystallise in elongated rhombs, and transmit light of a deep orange colour. (Found: N, 4·46; I, 38·96. $C_{14}H_{18}NI$ requires N, 4·28; I, 38·84 per cent).

Grateful acknowledgement is made of the grant of a research scholarship to one of us (D. P.) by the Government of Bihar. We also wish to express our thanks to Prof. L. M. Chatterjee of the Physics Department for help in recording the fluorescence and the sensitisation spectra.

SCIENCE COLLEGE, PATNA

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# THE EFFECT OF HYDROGEN-ION CONCENTRATION ON THE TIME OF SETTING OF THORIUM PHOSPHATE GEL-FORMING MIXTURES

By Miss A. Nathan

The investigation deals with the determination of the effect of the H-ion concentration on the time of setting. The time of setting of thorium phosphate gel-forming mixtures in all cases has been found at first to increase, then decrease and reach a minimum, followed by a rise, as the $p_H$ of the mixture is continuously decreased. The minimum time of setting takes place at lower and lower $p_H$ as the concentration of phosphoric acid in the mixture is decreased There is a linear relation between the amounts of phosphoric and hydrochloric acids corresponding to the minimum time of setting. $p_H$ and log $t$ curves are not straight lines as observed by Hurd and co-workers in the case of silicic acid gel-forming mixtures.

The effect of the addition of ethyl alcohol on the time of setting of gel-forming mixtures of different $p_H$ (those which set in minimum time and others which set before and after the minimum time) is of the same nature There is an increase in the time of setting, which reaches a maximum value and then falls as the amount of alcohol in the mixture is increased, the maximum has the lowest value for mixtures of $p_H$ corresponding to the minimum time of setting.

The mixtures set to a gel only when their $p_H$ values are less than 1·7, beyond this value a precipitate and not a gel is formed. No change in the $p_H$ of the mixtures takes place either on standing or on the addition of different amounts of alcohol.

The effect of hydrogen-ion concentration on the time of setting of gels has been studied most extensively in the case of gels of silicic acid. This effect was first pointed out by Holmes (*J. Phys. Chem.*, 1918, **22**, 570) who observed that silicic acid gels containing a very slight excess of OH-ions set in the shortest time and the time of setting rapidly increased with an increase in the H-ion concentration. He has also observed that there is a concentration of H-ion which delays the time of setting indefinitely and beyond this concentration the time of setting of the gel again becomes measurable and rapidly decreases to an immediate set. In the latter case he concludes that it is the dehydrating influence of the non-ionised molecules of acid which controls the time of setting. Prasad and Hattiangadi (*J. Indian Chem. Soc.*, 1929, **6**, 893) have also observed that the time of setting is minimum when the $p_H$ of the silicic acid gel-forming mixture is slightly higher than 7 and it is considerably increased in moderately acidic or highly alkaline mixtures. Ray and Ganguli (*J. Phys. Chem.*, 1930, **34**, 352) found that for each concentration of the alkali silicate solution there was a limiting range of $p_H$ value between which gel-formation took place.

Recently considerable amount of systematic work on the effect of $p_H$ on the time of setting of silicic acid gel-forming mixtures has been done by Hurd and co-workers. Hurd and Carver (*J. Phys Chem.*, 1933, **37**, 321) found that an increase in the $p_H$ of the silicic acid gel-forming mixture decreased the time of setting. Hurd, Raymond and Miller (*ibid.*, 1934, **38**, 668) have found that with gel-forming mixtures made up of sodium silicate and hydrochloric acid and having $p_H$ 4·2 to 5·5 and those made up of sodium silicate and acetic acid and having $p_H$ 4·14 to 6·0, the time of setting appears to be a linear function of the H-ion concentration. Hurd and Paton (*ibid.*, 1940, **44**, 57) have confirmed in a remarkable manner, the specific effect of H-ion concentration on the time of setting of silicic acid gels. On adding the same amount of extra acetic acid to the same silicic acid gel-forming mixture at different intervals from the commencement of the formation of the gel, they have shown that the setting of the gel proceeds at the same rate as without the addition of the extra acid, for the time before the acid is added, and subsequently at the rate followed in the presence of the extra acid added at the commencement of the setting.

Some observations on the effect of H-ion concentration on the time of setting are available in the case of other gels also. Freundlich and Sollner (*Kolloid Z.*, 1928, **44**, 309; **45**, 348) found that the time of setting of iron hydroxide gel increased from 82 seconds to 9000 seconds when the $p_H$ of the gel-forming system was changed from 3·86 to 3·11. Prasad, Mehta and Parmar (*Proc. Indian Acad. Sci.*, 1936, **3A**, 107) have found that the time of setting of mixtures giving rise to thorium phosphate gels is increased with the addition of sodium hydroxide of increasing concentration, while with the addition of increasing amounts of hydrochloric and nitric acids, the time of setting first diminished, reached a minimum and then increased and was again abruptly followed by a second minimum. With sulphuric acid there is only one minimum. Prasad and Desai (*J. Univ. Bom.* 1938, **7**, 132) have found that with the addition of increasing amounts of hydrochloric acid to thorium molybdate gel-forming mixtures, the time of setting first decreases, reaches a minimum and then increases and again decreases to a second minimum, followed by a rapid rise. Desai (unpublished work) found that the time of setting of thorium arsenate gel-forming mixtures first decreased, reached a minimum, and then increased as the quantity of hydrochloric acid in the mixture was increased. On plotting the logarithm of the time of setting against the logarithm of the concentration of hydrochloric acid, he found that the curves were made up of two intersecting straight lines.

In the present investigation the hydrogen ion concentration and the time of setting of thorium phosphate gel-forming mixtures containing various amounts of HCl have been studied systematically with a view to throwing light on the peculiar behaviour of acids observed by previous workers.

## EXPERIMENTAL

Hurd and Letteron's method (*J. Phys. Chem.* 1932, **36**, 604) was used in the present investigation for the measurement of the time of setting. The apparatus was placed in a thermostat kept at 35° ± 0·02°. The original device of Hurd and Letteron was improved upon by fixing a handle to the gear arrangement so that the supporting rod could be turned from without, thus obviating the necessity of opening the glass door of the thermostat. Another modification made was the fixing of a cross wire in front of the horizontal rod so that the latter could be brought back to its original position with reference to the former if the gel did not set.

*Preparation of Solutions.*—Thorium nitrate (6%) solution was prepared from Kahlbaum's pure thorium nitrate. The exact concentration of the solution was determined gravimetrically. The thoria content was found to be 2·800%, the theoretical amount being 2·875% for an $N/10$ solution. Phosphoric acid (approx. $2N$) solution was prepared from Merck's extra pure acid by weighing. It was then standardised and made exactly $2N$. Hydrochloric acid solution ($2N$) was prepared and used.

*Procedure.*—Thorium nitrate solution (5 c.c.) was measured out in each case in weighing bottles of the same dimensions. In test tubes were taken definite volumes of phosphoric acid and hydrochloric acid along with some distilled water to make up the total volume to 5 c.c. The contents of the weighing bottle were poured into the test tube and the mixture shaken for 15 seconds. It was then poured into the weighing bottle and gently inverted twice, and then allowed to set. This method of mixing was followed throughout the investigation.

It will be seen that an interval of 15 seconds has been allowed for shaking the mixture in every case. This time has not been counted in the time of setting, though strictly speaking this should be done. However, since it is the trend of results rather than the actual time of setting that is important, this has been left out. In most cases where the time of setting is of the order of several minutes, a uniform loss of time of an interval of a few seconds cannot make much difference and can be allowed for. On the other hand, when the time of setting is only a few seconds, the time occupied in shaking can assume serious proportions. This is the case only with mixtures containing 0·7 c c. of phosphoric acid, in which case the time of setting is extremely small. These results are, therefore, not very reliable. Their significance lies only in showing that even when the setting time is very small the same laws govern the progress of gelation.

TABLE I

Thorium nitrate = 5 c.c.

| | $x$=0·7* | $x$=0·6 | | $x$=0·55 | | $x$=0·5 | | $x$=0·4 | | $x$=0·3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HCl. | $t$ | $t$ | $p_H$. | $t$. | $p_H$. | $t$. | $p_H$ | $t$. | $p_H$. | $t$. | $p_H$. |
| 0·0 c·c. | 12″ | 8′20″ | 0·84 | 14′10″ | 0·95 | 36′ 0″ | 0·99 | 120′5″ | 1·06 | — | 1·19 |
| 0·1 | 16″ | 12′ 0″ | 0·79 | 16′ 0″ | 0·91 | 39′ 0″ | 0·90 | — | — | — | — |
| 0·2 | 9″ | 13′40″ | 0·71 | 18′30″ | 0·89 | 36′ 0″ | 0·89 | — | 0·83 | — | 0·94 |
| 0·25 | — | 11′15″ | 0·70 | — | — | — | — | — | — | — | — |
| 0·3 | — | 8′10″ | — | — | — | 33′20″ | 0·80 | — | — | — | — |
| 0·4 | — | 9′5″ | 0·69 | 16′ 0″ | 0·71 | 31′ 0″ | 0·76 | — | 0·72 | — | — |
| 0·5 | 13″ | 11′10″ | 0·64 | 14′30″ | 0·66 | 29′50″ | 0·73 | 64′45″ | 0·69 | — | 0·75 |
| 0·6 | — | — | — | 13′20″ | 0·63 | 28′40″ | 0·72 | — | 0·61 | — | — |
| 0·7 | — | — | — | 15′ 0″ | — | — | — | — | — | — | — |
| 0·8 | — | — | — | 16′ 0″ | 0·51 | 26′ 0″ | 0·60 | — | 0·55 | — | — |
| 1·0 | 18″ | 19′45″ | 0·50 | 22′ 0″ | 0·49 | 24′50″ | 0·50 | 55′40″ | 0·51 | 192′ | 0·53 |
| 1·2 | 23″ | — | — | — | — | 30′ 0″ | 0·39 | — | — | — | — |
| 1·3 | — | — | — | — | — | — | — | 53′15″ | — | 185′ | 0·47 |
| 1·4 | — | — | — | — | — | — | — | — | 0·40 | — | — |
| 1·5 | — | 25′ 5″ | 0·36 | 32′ 0″ | 0·37 | 40′10″ | 0·32 | 56′ 0″ | — | — | 0·38 |
| 1·7 | 26″ | — | — | — | — | — | — | — | — | — | — |
| 1·8 | — | — | — | — | — | — | — | — | 0·28 | — | — |
| 2·0 | — | — | — | — | — | — | — | 96′0″ | 0·25 | 177′ | 0·29 |
| 2·5 | — | — | — | — | — | — | — | — | — | 174′ | 0·20 |
| 3·0 | — | — | — | — | — | — | — | — | — | 184′ | 0·15 |
| 3·5 | — | — | — | — | — | — | — | — | — | 200′ | 0·11 |
| 4·0 | — | — | — | — | — | — | — | — | — | — | 0·05 |

* The $p_H$ values of the gel-forming mixtures containing 0·7 c c. of phosphoric acid are very low between 0·01 and 0·10.

TABLE II

| | | | | | |
|---|---|---|---|---|---|
| Phosphoric acid (c c ) | .. 0·60 | 0·55 | 0·50 | 0·40 | 0·30 |
| Hydrochloric acid (c c.) | ... 0·35 | 0·60 | 1·00 | 1·30 | 2·50 |

After mixing the constituents, the selected glass rod was inserted in the gel-forming mixture at about an angle of 20° to the vertical. It rested against the supporting rod of the arrangement described above. A slight movement of the rod determined whether the glass rod moved from its original position. If it moved, the supporting rod was again adjusted by turning the handle to bring the glass rod back to the original position. The accuracy of these measurements was increased by repeating the observations several times, and each time disturbing the mixture as little as possible by shifting the rod only when the gel was about to set. The diameter of the glass rod used to measure the time of setting of gel-forming mixtures containing 0·40 c.c. to 0·70 c.c. of phosphoric acid was 0·094 cm., and for the mixtures containing 0·30 c.c. of phosphoric acid, it was 0·062 cm. The reason for using a rod of a smaller diameter in the latter case is that when the amount of phosphoric acid is low, the gel formed is not firm enough to support a heavier rod thus rendering it difficult to locate the exact time of setting.

Increasing amounts of hydrochloric acid were added to several sets of the gel-forming mixtures containing the same amount of thorium nitrate and increasing amounts of phosphoric acid. The concentration of hydrochloric acid was varied from 0·2 to 3·0 c.c. of 2*N* solution and that of phosphoric acid from 0·3 to 0·7 c.c. of 2*N* solution. The total volume in every case was 10 c.c.

The H-ion concentration was measured by a $p_H$ electrometer manufactured by Becker and Co., Ltd. The instrument was at first adjusted in accordance with the instructions supplied with it. The constituent of the various gel-forming mixtures were mixed and shaken in a test tube and then the mixture was poured into the glass dish provided for the purpose.

The results obtained are given in Table I. They represent the mean of several readings which did not differ from each other by more than 2 to 5 seconds. This accuracy was obtained only after the modifications described above were introduced in the apparatus. In the table, $x$ represents the volume in c.c. of the phosphoric acid solution and $t$, the time of setting in minutes.

## DISCUSSION

It will be seen from the foregoing results that with the addition of increasing amounts of hydrochloric acid, the time of setting of thorium phosphate gels first slightly increases, and then decreases and reaches a minimum and subsequently increases fairly rapidly. The slight rise in the beginning is very definite, and is not shown in the last two columns of the table, not because it does not exist, but because the time of setting of the gel-forming mixtures corresponding to this point is high and inconvenient to measure.

These results are similar to those obtained by Parmar, Mehta and Prasad (*loc. cit.*). The minimum amount of 4*N*-HCl used by these workers is 0·5 c.c. while the amounts used by the author range from 0·10 to 3·5 c.c. of 2*N*-HCl or 0·05 to 1·75 c.c. of 4*N*-HCl. This explains why Parmar, Mehta and Prasad missed the first rise observed by the author. The decrease in the time of setting after the second rise observed by Parmar, Mehta and Prasad could not be observed in this case as this occurs in the presence of 1 5 c.c. of 4*N*-HCl in the mixture containing 5·0 c.c. of thorium nitrate solution and 0·7 c.c. of the solution of phosphoric acid, while the highest amount of 2*N*-HCl used in this investigation in this mixture is 2·0 c.c.

### *The Minimum Point.*

It will be seen from Table I that greater amounts of HCl are required to cause a gel-forming mixture to set in minimum time as the concentration of phosphoric acid in the mixture is decreased. The amounts of phosphoric acid and hydrochloric acid corresponding to the minimum time of setting are shown in Table II.

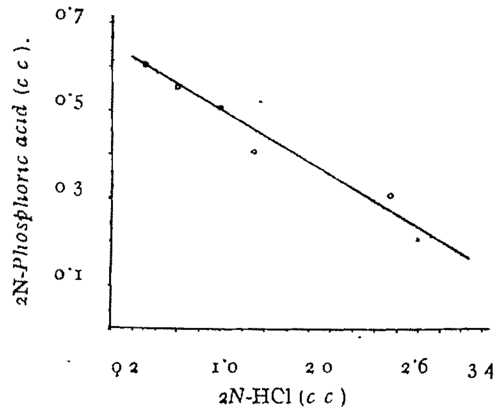
On plotting the amounts of phosphoric acid ($x$) and hydrochloric acid ($y$) from Table II a straight line (shown in Fig. 1) is obtained. This shows that effect of the two acids is complementary. On measuring the slope of the line, it is found that it can be expressed by the equation

$$y=4-6x$$

$$\text{or } x=\frac{4-y}{6}.$$

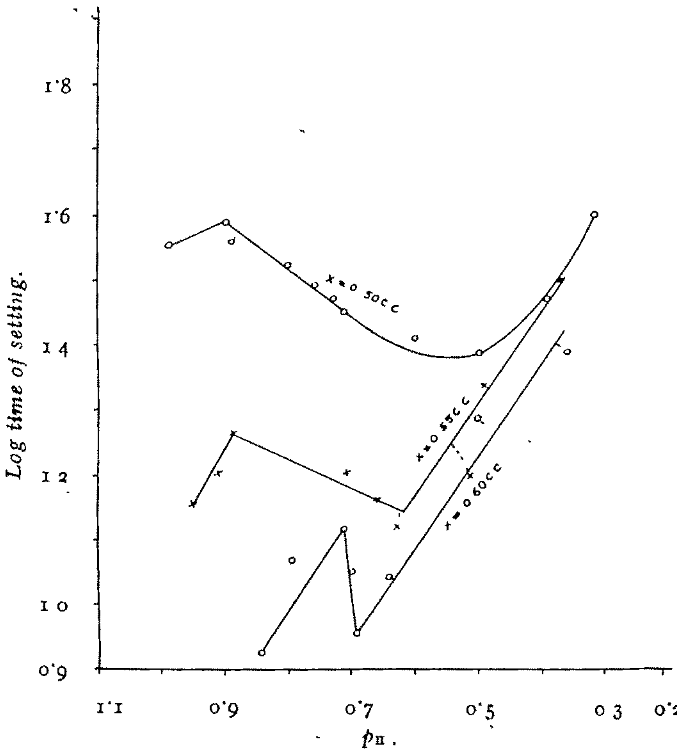
This relation can be used to predict the amount of hydrochloric acid to be added to a mixture containing 5 c.c of thorium nitrate solution and any given quantity of phosphoric acid to cause the mixture to set in the minimum time.

FIG. 1.



*Effect of Phosphate-ion Concentration.*—Various workers have observed that the time of setting of a gel varies with a change in the concentration of the constituents of a gel-forming mixture. In the case of gels of inorganic substances, it has been usually found that their time of setting (*cf.* Prakash and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 587; Parmar, Mehta and Prasad, *loc. cit.*; Prasad and Desai, *loc. cit.*) increases on decreasing the concentration of the salt carrying the acid ion of the gel forming substance. The results obtained in this investigation are in agreement with those observed by previous workers.

FIG. 2



*Effect of $p_H$ on the Time of Setting.*—The effect of $p_H$ on the time of setting of various mixtures can be seen from Table I. On plotting $p_H$ values against the logarithm of time of setting, curves shown in Fig. 2 for mixtures containing 0·50, 0·55 and 0·60 c.c. of phosphoric acid are obtained. These curves are practically of the same nature as the curves obtained by plotting the c.c. of HCl solution added to the gel-forming mixtures against time. The linear relation between the time of setting and H-ion concentration observed by Hurd and co-workers is not observed in this case. It will be observed that the variations in the $p_H$ values of the mixtures studied in this investigation are not great.

It will be noted from Table I that the highest $p_H$ value of the several gel-forming mixtures used in this investigation is 1·19 In order to prepare gel-forming mixtures of $p_H$ higher than this, sodium hydroxide instead of hydrochloric acid was added to the mixture of thorium nitrate and phosphoric acid. For this purpose different volumes of 1·0 $N$-NaOH were added to 5·0 c.c. of 2$N$-phosphoric acid and the total volume was made up to 5·0 c.c. by the additition of water in the manner described before and the time of setting was measured by Fleming's method (*Z. Physik*, 1902, **41**, 427). $p_H$ values were measured immediately after mixing the solutions with the glass electrode. The results obtained are given in the following table.

TABLE III

Thorium nitrate = 5 c.c. Phosphoric acid = 0·5 c.c.

| 1·0 $N$-NaOH. | Time of setting. | $p_H$. | Remarks. |
|---|---|---|---|
| 0·0 c.c. | 24 min. | 0·99 | Clear solution set to a transparent gel |
| 0·1 | 29 | 1·01 | Flocculent precipitate disappears on setting |
| 0·2 | 41 | 1·11 | Do. |
| 0·5 | 46 | 1·24 | Do |
| 1·0 | — | 1·72 | Precipitate formed. |

It will be seen that the relationship between the $p_H$ value and the time of setting of the above mixtures follows a regular curve within the $p_H$ range studied. The highest point on the curve corresponds to the $p_H$ value beyond which gel-formation does not take place, for instance when the $p_H$ value of the gel-forming mixture is 1·7, only a precipitate is formed. This value may therefore be taken as the limiting value beyond which no gel-formation takes place.

If the results given in Table III are considered along with those given in Table I for the mixture containing 0·5 c.c. of phosphoric acid, and due allowances are made for the differences in the time of setting determined by the methods of Hurd and Fleming (*loc. cit.*) it will appear that with a regular decrease in $p_H$, the time of setting of this mixture undergoes a number of significant changes. It first decreases and reaches a first minimum which will probably be the mixture to which no acid or alkali is added. It then increases to a small extent and reaches a maximum value. It again decreases, and reaches a second minimum after which it again rises to a fairly high value. It will be observed that the interval between the first minimum and maximum becomes more pronounced as the amount of phosphoric acid in the gel-forming mixture is increased.

*Effect of Time on the $p_H$ of a Gel-forming Mixture.*—It was observed that no change in $p_H$ takes place during the gelation of all gels studied in this investigation. These results confirm the observations of Prasad and Desai (*J. Univ. Bom.*, 1938, **7**, 132).

*Effect of the Addition of Ethyl Alcohol on the Time of Setting and $p_H$ of Gel-forming Mixtures containing different amounts of* HCl —It has been found that the effect of the addition of non-electrolytes on the time of setting of gels depends upon the nature of the gel. Prasad and Hattiangadi (*J. Indian Chem. Soc.*, 1929, **6**, 991) found that the addition of increasing amounts of alchohol to the silicic acid gel-forming mixtures decreases the time of setting in alkaline medium but if the gel-forming mixture is even slightly acidic, it is delayed considerably.

Munro and co-workers (*Canadian J. Res.*, 1937, **15**, 353; 1938, **16**, 390; 1939, **17**, 266, 404) examined the effect of several polyhydric alcohols on the time of setting of silicic acid gels. They found that the time of setting of alkaline gels decreased with the addition of a series of monohydric alcohols Further they found that there was a certain $p_H$ of the gel-forming mixtures at which the action of alchohols changed from retarding to an accelerating one.

The effect of the addition of increasing quantities of ethyl-alcohol on the time of setting of certain mixtures of phosphoric and hydrochloric acids with thorium nitrate was therefore studied. These mixtures correspond to the minimum time of setting as well as before and after the minimum time of setting. The particular gel-forming mixtures on which the effect of increasing amounts of alcohol was studied were those containing (*i*) 0·6 c.c. phosphoric acid and 0·30, 0·25 and 0·50 c c. of HCl and (*ii*) 0·5 c.c. phosphoric acid and 0·40, 1·00 and 1·20 c.c. of HCl.

The general effect of the addition of ethyl alcohol to various mixtures is similar in all cases. This can be seen from Table IV.

TABLE IV

Thorium nitrate = 5·0 c.c Phosphoric acid = 0·6 c.c. Hydrochloric acid = 0·5 c.c. Temp. = 35°.

| Alcohol (c.c.) | ... 0·0 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 1·2 | 1·5 | 2·0 |
|---|---|---|---|---|---|---|---|---|---|
| Setting time | ... 11′0″ | 11′30″ | 11′40″ | 12′0″ | 13′40″ | 10′30″ | 9′30″ | 9′20″ | 9′0″ |
| $p_H$ | ... 0·62 | 0·62 | 0·62 | 0·62 | 0·62 | 0·62 | 0·62 | 0·62 | 0·62 |

Thus with the addition of increasing amounts of alcohol to all the gel-forming mixtures the time of setting first increases, reaches a maximum value and then decreases, the maximum value depending upon the HCl content of the mixture. It has the lowest value for mixtures containing HCl corresponding to the minimum time of setting. This leads one to conclude that the maximum time of setting in the presence of alcohol decreases and reaches the lowest value as the amount of HCl in the gel-forming mixture reaches that corresponding to the minimum time of setting.

Although no definite information regarding the nature of the different gel-forming mixtures or set gels can be obtained from results of these experiments, it can be surmised that the structure of the gels obtained from mixtures containing HCl in amounts lower and higher than that corresponding to the minimum time of setting are essentially different. This view is substantiated from the visual observation of various gels obtained in the presence of alcohol.

It will be observed that the $p_H$ of the gel-forming mixtures does not change with the addition of alcohol. The addition of alcohol, may, therefore, cause changes only in the rate of formation of the colloidal particles in the gel-forming mixture or in the rate of formation of ultimate particles of the gel.

The author feels grateful to Dr. Mata Prasad, D.Sc., F.I.C., for suggesting the problem and for guidance throughout the progress of this work.

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# THE TIME OF SETTING AND CHANGES IN H-ION CONCENTRATION DURING THE SETTING OF GELS FORMED BY THE INTERACTION OF OPPOSITELY CHARGED SOLS. PART II. THE INTERACTION OF NICKEL HYDROXIDE AND MANGANESE DIOXIDE SOLS WITH ALUMINIUM HYDROXIDE SOL

By Mata Prasad and S. D. Mehta

The time of setting of the gels obtained by mixing negatively charged sols of (*i*) nickel hydroxide and (*ii*) manganese dioxide with positively charged sol of aluminium hydroxide has been measured at 35°. The relation $t=Ra^{-n}$ is found to hold between the time of setting ($t$) and the volume ($a$), of the oppositely charged sols No appreciable changes in $p_H$ take place during the formation of these gels .

It is well known that mutual coagulation takes place when oppositely charged sols are mixed together in suitable proportions Prasad and Mehta (*Current Sci* , 1943, **12**, 19) have found that when oppositely charged sols of suitable concentrations are mixed together under certain conditions, gel-formation takes place. Attempts have, therefore, been made to determine whether the formation of gels by this method follows the same behaviour as observed with gels prepared by other methods.

This investigation deals with the determination of the time of setting and the changes in the H-ion concentration taking place during the setting of the gels formed by mixing the negatively charged sols of (*i*) nickel hydroxide and (*ii*) manganese dioxide, with the positively charged sol of aluminium hydroxide

## EXPERIMENTAL

*Preparation of the Aluminium Hydroxide Sol.*—Aluminium hydroxide sol was prepared by Crum's method and its colloidal content was found to correspond to 0·235 g. of $Al_2O_3$ per 100 c.c. of the sol.

*Preparation of the Nickel Hydroxide Sol.*—It was prepared by a method found by the authors. Nickel hydroxide precipitated by the addition of approximately 2·0*N*-NaOH solution to a 10% solution of nickel chloride was washed free from chloride ions and then dissolved in 30 g. of tartaric acid. The required amount of 2·0 *N*-NaOH was then added to the clear solution which rapidly set to a clear transparent gel which on shaking with distilled water dispersed completely and gave rise to the transparent green-coloured stable sol. It was negatively charged and its colloidal content corresponded to 0·301 g. of nickel per 100 c.c. of the sol.

*Preparation of Manganese Dioxide Sol.*—It was prepared by the reduction of potassium permanganate with sodium arsenite and its colloidal content corresponded to 0·057 g. of $MnO_2$ per 100 c.c. of the sol.

*Method of Measuring the Time of Setting.*—The time of setting was measured at 35°, in an air thermostat by Hurd and Letteron's method (*J. Phys. Chem.*, 1932, **36**, 604) in which certain modifications were introduced for the sake of accuracy.

*Procedure.*—A number of test tubes were filled with 5 c.c. of the aluminium hydroxide sol. In another set of test tubes different known volumes of the oppositely charged sols were taken and diluted with distilled water so as to make up their volume to 5 c.c. Both sets of test tubes were put in the air thermostat to attain the constant temperature. The two sols were then mixed a number of times and well shaken. The mixture was then immediately transferred to a small weighing bottle, and a glass rod 3″ long and 1 mm. in diameter was inserted in position; a stop-watch was also started simultaneously. The time required for the glass rod to remain in position when the supporting rod is removed is the time of setting of the gel. To increase the accuracy of the measurements a number of readings were taken, each time disturbing the gel-forming mixture as few times as possible. The minimum time obtained in this manner was taken as the time of setting of the gel.

The small volumes of the oppositely charged sols were measured out from a micro-pipette measuring up to 0·01 c.c The results obtained are given in the following tables in which $a$ = c.c. of the oppositely charged sol, and $t$ = time of setting in minutes.

TABLE I

*Nickel hydroxide sol.*

$m = 36·66$. $\log R = -3·50$.

| $a$. | $t$. | log $a$. | log $t$ (obs.). | log $t$ (calc.). |
|---|---|---|---|---|
| 0·80 | 1·0 | −0·0969 | 0·0000 | 0·052 |
| 0·79 | 1·5 | −0·1024 | 0·1761 | 0·254 |
| 0·78 | 3·0 | −0·1079 | 0·4771 | 0·457 |
| 0·77 | 5·0 | −0·1135 | 0·6990 | 0·661 |
| 0·76 | 8·0 | −0·1192 | 0·9031 | 0·870 |
| 0·75 | 13·0 | −0·1249 | 1·1139 | 1·078 |
| 0·74 | 19·0 | −0·1308 | 1·2788 | 1·294 |
| 0·73 | 27·0 | −0·1367 | 1·4314 | 1·512 |

TABLE II

*Manganese dioxide sol.*

$m = 10·24$. $\log R = 4·20$.

| $a$. | $t$. | log $a$. | log $t$ (obs.). | log $t$ (calc.). |
|---|---|---|---|---|
| 2·50 | 1·5 | 0·3979 | 0·1761 | 0·123 |
| 2·40 | 2·0 | 0·3802 | 0·3010 | 0·305 |
| 2·30 | 3·0 | 0·3617 | 0·4771 | 0·491 |
| 2·20 | 5·0 | 0·3424 | 0·6990 | 0·693 |
| 2·10 | 8·0 | 0·3222 | 0·9031 | 0·894 |
| 2·00 | 12·5 | 0·3010 | 1·0969 | 1·116 |
| 1·90 | 22·5 | 0·2788 | 1·3522 | 1·347 |
| 1·80 | 35·0 | 0·2553 | 1·5502 | 1·584 |

*Measurement of $p_H$ during Gel-formation.*—The H-ion concentration of the two gel-forming mixtures from each set were measured by means of Coleman's electrometer at various intervals during and after setting until no change was observed. For this purpose 5 c.c. of the aluminium hydroxide sol were taken in one test tube and in another were taken the selected volumes of the oppositely charged sols and distilled water to make up the volume to 5 c.c.. The contents of the two test tubes were mixed together and well shaken and the mixture was introduced in the electrometer; a stop-warch was also started at the same time. The electrometer was standardised and occasionally checked by means of standard buffer solutions. The results obtained are given in the following table in which $t$ represents the time in minutes after introducing the gel-forming mixture in the electrometer, at which the $p_H$ readings were taken.

TABLE III

| $t$. | 1·0 | 2·5 | 5·0 | 7·5 | 10·0 |
|---|---|---|---|---|---|
| | | 0·74 C.c. of nickel hydroxide sol. | | | |
| $p_H$ | 4·10 | 4·10 | — | — | — |
| | | 0·75 C.c. of nickel hydroxide sol. | | | |
| $p_H$ | 4·06 | 4·06 | 4·07 | 4·08 | 4·08 |
| | | 1·80 C.c of manganese dioxide sol. | | | |
| $p_H$ | 3·89 | 3·90 | 3·90 | — | — |
| | | 2·00 C.c. of manganese dioxide sol. | | | |
| $p_H$ | 3·96 | 3·96 | — | — | — |

## DISCUSSION

The gels formed in the presence of both the nickel hydroxide and manganese dioxide sols are quite transparent and thixotropic. It is therefore clear that all the conditions (*cf.* Prasad, Presidential Address, *Ind. Sci. Cong.*, 1940) required for the formation of gels prepared by other methods, are satisfied in the mode of gel-formation described in this paper.

It will be seen that the time of setting of gels decreases at first rapidly and then slowly as increasing quantities of the oppositely charged sols are added to the same volume of the aluminium hydroxide sol. These results are of the same nature as those obtained in the case of gels prepared by the addition of electrolytes and by mixing the oppositely charged sols of ferric and aluminium hydroxides to the nickel hydroxide sol (Prasad and Mehta, *loc. cit.*).

On plotting log $a$ against log $t$, the curves obtained are straight lines. Same results have bean obtained in the case of gels prepared by (*i*) the addition of electrolytes to sols by Dube and Prakash (*Proc. Ind. Acad. Sci.*, 1940, **11**, 331) and (*ii*) mixing oppositely charged sols by Prasad and Mehta (*loc. cit.*). This confirms the conclusion that the formation of gels by mixing oppositely charged sols is similar to that obtained by other methods. Further the relation between $a$ and $t$ is given by $t=Ra^{-m}$, in which $m$ and $R$ are constants. This expression is of the same type as put forward by Prasad and Hattiangadi (*J. Indian Chem. Soc.*, 1927, **6**, 653) and by Dube and Prakash (*loc. cit.*).

The values of $m$ and log $R$ calculated from any two values of $a$ and $t$ in a particular set of results are given at the top of each table. It will be seen that they are different in each case.

These values of $m$ and $R$ have been used for calculating the values of $t$ for the various values of $a$ employed in this investigation and the results obtained are given in the fifth columns of Tables I and II. A comparison of the calculated and observed values of $t$ shows that the expression $t=Ra^{-m}$ reproduces the experimental results fairly accurately.

The $p_H$ values of various gel-forming mixtures do not increase appreciably as happens during the setting of several inorganic gels studied by Prakash and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 391) and Prasad and Mehta (*loc. cit.*).

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# MAGNETIC EVIDENCE REGARDING THE VALENCY OF COLOURANT IONS IN GLASS PART II.

By N. A. Yajnik, Ram Chand and D. C. Jain

Valency and the state of iron ions in glasses prepared by using borax and microcosmic salt have been determined with the aid of chemical analysis and magnetic susceptibility measurements. Conditions of iron oxide as such corresponding to different colours in glasses have been shown

Two papers have already been published from this laboratory regarding the nature of colourant ions in glass (Bhatnagar, *Nature*, 1939, **143**, 599 ; Bhatnagar, Khosla and Ram Chand, *J. Indian Chem. Soc.*, 1940, **17**, 515) in which the authors have investigated the state of manganese, cobalt and nickel in phosphate glasses. Magnetic susceptibility measurements have been used to find out the valency and the state of colourant ions.

Iron is another element which has been used for colouring glasses and glazes and it has been claimed to impart all the colours of spectrum to them (*cf.* Bancroft and Cunningham, *J. Phys. Chem.*, 1930, **34**, 1). But it is usually employed to give yellow and green colours.

Bancroft and Cunningham (*loc. cit.*) have used different amounts of boric acid and alkalis to prepare the glasses and have concluded that iron in the reduced state gives green colour, while in the oxidised condition the colour is yellow.

In the present investigation borax as well as microcosmic salt have been used to prepare the glasses. With the aid of chemical analysis and magnetic susceptibility measurements the valency and the state of iron ions, as well as the condition of iron oxide as such corresponding to different colours, have been shown.

Magnetic susceptibility of iron ions in different states of valency has been calculated by Stoner and Van Vleck formula.

$$\chi_M = \frac{n\beta^2}{3kT}\left[4\,s(s+1) + l\,(l+1)\right]$$

where $s$ and $l$ are spin and orbital moments.

Guoy type balance was used to find the magnetic susceptibilities. The same technique was followed to prepare the glasses as by Bhatnager, Khosla and Ram Chand (*loc. cit.*).

In the case of borax glasses iron imparted a yellow colour in oxidising and green in reducing conditions, when cold. In the case of microcosmic glasses yellowish brown and greenish brown colours were obtained in corresponding conditions.

Table I

| Total iron. | $Fe^{II}$ in total iron. | $\chi_M$glass $\times 10^6$ | $\chi_M$ (Fe) ionic $\times 10^6$. obs. | calculated with $l$ operative. | quenched. | Total iron. | $Fe^{II}$ in total iron | $\chi_M$glass $\times 10^6$ | $\chi_M$ (Fe) ionic obs. | calculated with $l$ operative. | quenched. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Reduced microcosmic glasses | | | | | | Oxidised microcosmic glasses | | | | | |
| 1·771% | 14·41% | 4·070 | 251·8 | 260·1 | 253·4 | 1·795 | 3·70 | 4·263 | 260·3 | 264·1 | 262·2 |
| 2·621 | 17·30 | 6·167 | 250·0 | 259·0 | 251·0 | 1·121 | 7·95 | 2·510 | 258·7 | 262·4 | 258 8 |
| 2·183 | 13·08 | 5·250 | 253·1 | 260·6 | 254·5 | 2·100 | 2·10 | 5·062 | 259·4 | 264 7 | 263·4 |
| 1·950 | 15·00 | 4·528 | 252·0 | 259·8 | 253·0 | 3·010 | 2·90 | 7·464 | 260·6 | 264 3 | 263·0 |
| Oxidised borax glasses | | | | | | Reduced borax glasses | | | | | |
| 1·189 | ... | 2·704 | 262·4 | — | — | 1·019 | 33·02 | 2·030 | 240·1 | 253·0 | 237·9 |
| 1·024 | — | 2·317 | 266·9 | — | — | 1·189 | 55·90 | 2·200 | 220 0 | 244 2 | 218 7 |

Total iron was estimated by reduction to ferrous state with stannous chloride and hydrochloric acid and titration with dichromate solution. Ferrous content of glasses was estimated by dissolving a known weight of the glass in a known volume of standard permanganate solution in cold, and back-titrating with standard ferrous sulphate solution.

In the case of ferrous state $l$ moment can be operative as well as quenched. Therefore $\chi_M$ (ionic) has been calculated for both these conditions and the results tabulated along with the results obtained from actual experimental data.

Magnetic susceptibilities (observed and calculated) and results of analyses of various types of glasses are given in Table I.

TABLE II

*Susceptibility values obtained at different temperatures.*

$\theta = 2{\cdot}5$ abs.

| Temp. | — | 289° | 315° | 359° | 421° | 470° |
|---|---|---|---|---|---|---|
| $\chi_M \times 10^6$ | ... | 262·4 | 231·0 | 202·3 | 171·8 | 155·4 |
| $C_M$ | .. | 4·198 | 4·125 | 4·027 | 4·015 | 4·056 |

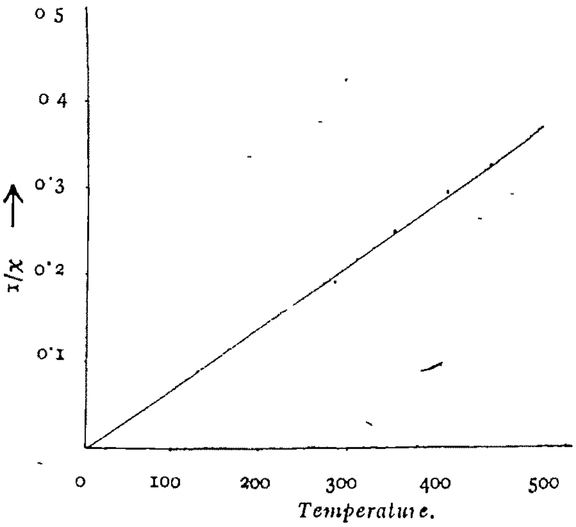
Mean value for $C_M = 4.084$.

$\mu_B = 5{\cdot}74$.

Calculating the ionic susceptibilities of iron from Stoner-Van Vleck formula, $\chi_M$ (ionic) for $Fe^{III}$ ions which are in $^6S_{5/2}$ state is $265{\cdot}5 \times 10^{-6}$ at 25° $\chi_M$ ionic for $Fe^{II}$ ions which are in $^5D_4$ state *i.e.*, $l = 2$ and $s = 3$ is $182{\cdot}0 \times 10^{-6}$ at 25° where $l$ is quenched and $227{\cdot}5 \times 10^{-6}$ at 25° where $l$ is operative.

Calculating the ionic susceptibility of iron from the analytical data and comparing it with the observed values in Table I, we find that values obtained when $l$ moment is quenched agree better with observed values than when it is operative. It has been noted by Sommerfield ("Atombau" 4th Ed. p. 631), Bose (*Z. Physik*, 1927, **43**, 864), and Stoner (*Phil. Mag.*, 1929, **8**, 250) that in the case of ions of the iron group $l$ moment is fully quenched.

A borax glass prepared in the oxidising atmosphere was tried at various temperatures to get the value of Bohr magneton for ferric ions. Results are tabulated in Table I. Curie point has been determined by plotting $1/\chi$ and $T$ and reading the intercept on $T$ axis. $\theta = 2{\cdot}3$ and $\mu_B = 5{\cdot}74$ which agrees fairly well with the theoretical value 5·9 for trivalent iron where $l$ is quenched.



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# KOSTANECKI-ROBINSON REACTION. PART V. BENZOYLATION OF SOME *o*-HYDROXY KETONES

By P. L. Trivedi, S. M. Sethna and R. C. Shah

3-Benzoylflavone derivatives have been isolated in the Kostanecki-Robinson benzoylation of resacetophenone, 2-acetylresorcinol and phloracetophenone by using the experimental technique developed by Sethna and Shah.

In a previous paper Sethna and Shah (*J. Indian Chem. Soc.*, 1940, **17**, 601) benzoylated orcacetophenone and in the course of this work, developed a new technique of working up the benzoylated product which enabled them to isolate the 3-benzoylflavone derivative formed.

Their experimental technique consists in treating the reaction mixture after benzoylation with petroleum ether and water to remove benzoic anhydride and sodium benzoate respectively which makes possible the isolation of flavones with both the *O*- and the *C*-benzoyl groups intact. The *O*-benzoyl group can then be removed smoothly by the use of concentrated sulphuric acid, leaving the 3-benzoyl group intact. This new technique has now been employed for the isolation of 3-benzoylflavones in the case of benzoylation of other *o* hydroxy-ketones. A slight modification introduced by the present authors is the use of carbon disulphide in the place of petroleum ether.

Resacetophenone 2-acetylresorcinol and phloracetophenone have been benzoylated and the reaction mixture treated with carbon disulphide and water to remove benzoic anhydride and sodium benzoate respectively and 7-benzoyloxy-3-benzoylflavone, 5-benzoyloxy-3-benzoylflavone and 5 : 7-dibenzoyloxy-3-benzoylflavones have been isolated. These on treatment with concentrated sulphuric acid give 7-hydroxy 3-benzoylflavone, 5-hydroxy-3-benzoylflavone and 5 : 7-dihydroxy-3-benzoylflavone respectively. The 3-benzoylflavones may be debenzoylated by treatment with alcoholic potash. The method of Sethna and Shah has, therefore, been found to be of general applicability in the isolation of 3-benzoylflavones in the Kostanecki-Robinson benzoylation of *o*-hydroxy-ketones.

## EXPERIMENTAL

*Benzoylation of Resacetophenone : 7-Benzoyloxy-3-benzoylflavone.*—An intimate mixture of resacetophenone (2 g.), sodium benzoate (6 g.) and benzoic anhydride (20 g.) was heated in an oil-bath at 180-190° for 10 hours. The reaction product was extracted with about 100 c.c. of carbon disulphide to remove benzoic anhydride and the residue thoroughly washed with water to remove sodium benzoate. It was finally treated with sodium bicarbonate and then with water. The crude product crystallised from alcohol-acetone mixture (1 : 1) in long needles (1 g.), m.p. 167°. Baker (*J. Chem. Soc.*, 1933, 1381) gives the same m.p. The product is insoluble in alkali.

*7-Hydroxy-3-benzoylflavone.*—The above dibenzoylflavone (0·8 g.) was kept in contact with concentrated sulphuric acid (10 c.c.) overnight. The solution was poured into cold water and the product was crystallised from alcohol in prisms (0·4 g.), m.p. 264-65°. Rangaswamy and Seshadri (*Proc. Indian Acad. Sci.*, 1939, **10A**, 6) give m.p. 265°. It readily dissolves in cold dilute alkali giving a pale yellow solution.

*7-Hydroxyflavone.*—7-Hydroxy-3-benzoylflavone (1 g.) was refluxed with alcoholic potash (10%, 15 c.c.) for ½ hour. The excess of alcohol was distilled off and the solution acidified with dilute hydrochloric acid, when a product separated which was crystallised from alcohol in long colourless needles (0·6 g.), m.p. 240°. Rangaswami and Seshadri (*loc. cit.*) and Baker (*loc. cit.*) give the same m.p.

*Benzoylation of 2-Acetylresorcinol*: *5-Benzoyloxy-3-benzoylflavone.*—An intimate mixture of 2-acetylresorcinol (2 g.), sodium benzoate (6 g.) and benzoic anhydride (20 g.) was heated in an oil-bath at 180-90° for 9 hours. The fused mass was powdered, extracted with carbon disulphide, then thoroughly washed with water and the residue then washed with dilute sodium bicarbonate solution and then with water as in the previous case. The product was crystallised from acetone in yellow plates (0·9 g.), m.p. 234-35°. It is insoluble in cold dilute alkali. (Found : C, 79·9 ; H, 4·7. $C_{28}H_{18}O_4$ requires C, 80·4 ; H, 4·3 per cent).

*5-Hydroxy-3-benzoylflavone.*—The above dibenzoylflavone (1 g.) was kept in contact with concentrated sulphuric acid (10 c.c.) overnight. The product obtained on pouring this into cold water was crystallised from ethyl acetate in yellow prisms (0·7 g.), m.p. 174-75°. Sugasawa (*J. Chem. Soc.*, 1934, 1483) gives m.p. 174°.

*5-Hydroxyflavone.*—5-Hydroxy-3-benzoylflavone (1 g.) was refluxed with alcoholic potash (10%, 15 c.c.) for ½ hour and the product obtained on working up as before was crystallised from alcohol in thin yellow needles (0·6 g.), m.p. 156-57°. Sugasawa (*loc. cit.*) gives m.p. 157°.

*Benzoylation of Phloracetophenone* : *5 : 7-Dibenzoyloxy-3-benzoylflavone.*—An intimate mixture of phloracetophenone (2 g.), sodium benzoate (6 g.) and benzoic anhydride (20 g.) was heated in an oil-bath for 8 hours at 180-90°. The fused mass was extracted with carbon disulphide, the residue was thoroughly washed with water and then washed with dilute sodium bicarbonate solution and finally with water. The crude product, thus obtained, was crystallised from alcohol-acetone mixture (1 : 1) in tiny white needles (1·3 g.), m.p. 167-68°. It is insoluble in cold dilute alkali. (Found : C, 76·0 ; H, 4·0. $C_{36}H_{22}O_7$ requires C, 76·3 ; H, 4·1 per cent).

*5 : 7-Dihydroxy-3-benzoylflavone.*—The above flavone (0·8 g.) was kept in contact with concentrated sulphuric acid (10 c.c.) overnight and the resulting product on pouring in cold water was crystallised from dilute alcohol (50%) in small prisms (0·5 g.), m.p. 145-46°. It is readily soluble in cold dilute alkali giving a yellow solution. (Found : C, 73·4 ; H, 4·3. $C_{22}H_{14}O_5$ requires C, 73·7 ; H, 3·9 per cent).

*5 : 7-Dihydroxyflavone* (Chrysin).—5 : 7-Dihydroxy-3-benzoylflavone (1 g.) was refluxed with alcoholic potash (10%, 15 c.c.) for ½ hour and the product obtained on working up the reaction mixture as before, was crystallised from alcohol in small prismatic needles (0·6 g.), m.p. 274-75°. Robinson and Venkataraman (*J. Chem. Soc.*, 1926, 2347) give m.p. 275°.

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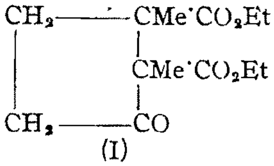
# ACTION OF SODIUM ON ETHYL β-METHYLBUTANE-αβδ-TRICARBOXYLATE
## PART I

BY RAM NARAYAN CHAKRAVARTI

Contrary to the observations of Baker (*J. Chem. Soc.*, 1931, 1548), it is now found that ethyl 4-methyl*cyclo*pentan-1-one-2 :4-dicarboxylate constitutes the chief product of the sodium condensation of ethyl β-methylbutane-αβδ-tricarboxylate.

The subject matter of the present investigation originated in some experiments which were carried out with the object of synthesising the keto-ester (I).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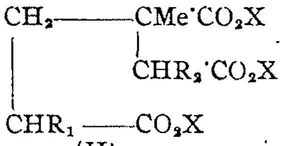
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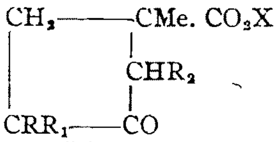

(III)

A convenient starting point for this purpose appeared to be provided by ethyl β-methylbutane-αβδ-tricarboxylate (II, $R_1=R_2=H$; $X=Et$), which was first prepared by Ruzicka (*Ber.*, 1917, **50**, 1362) in connection with his well known synthesis of fenchone.

The Dieckmann cyclisation of (II, $R_1=R_2=H$; $X=Et$) can obviously occur in two ways, giving the *cyclo*pentanone esters (III, $R_1=R_2=H$; $R=CO_2Et$; $X=Et$) and (III, $R=R_1=H$; $R_2=CO_2Et$; $X=Et$). Ruzicka did not, however, consider it necessary to determine the constitution of this ester, since, on hydrolysis either structure would yield 3-methyl*cyclo*penten-1-one-3-carboxylic acid (III, $R=R_1=R_2=X=H$), which was the required intermediate in the fenchone synthesis.

Baker (*J. Chem Soc.*, 1931, 1548) appears to have established definitely that the initial conensation product must be represented by (III, $R=R_1=H$; $R_2=CO_2Et$; $X=Et$), since on careful oxidation with potassium permanganate it gave α-methylglutaric acid, a liquid acid, analysis of the silver salt of which corresponded with that of α-hydroxy-α-methylglutaric acid, and a trace of succinic acid. No trace of either β-methyltricarballylic acid or of methylsuccinic acid, the products which would result from the oxidation of an ester of structure (III, $R_1=R_2=H$; $R=CO_2Et$; $X=Et$) could be detected.

It was, therefore, hoped that the products of the sodium condensation of (II, $R_1=R_2=H$; $X=Et$) on treatment with methyl iodide would afford the desired keto-ester (I). Curiously enough the methylated keto-ester actually isolated from the products of the above condensation on hydrolysis with alcoholic potash yielded β-methylpentane-αβδ-tricarboxylic acid (II, $R_1=Me$; $R_2=H$; $X=H$), m.p. 178-79° (*phenylphenacyl* ester, m.p. 158°), identical with a synthetic specimen described below. It follows, therefore that the methylated keto-ester should be best represented by the structure (III, $R=Me$; $R_1=CO_2Et$; $X=Et$; $R_2=H$). Moreover, the latter on treatment with sodium ethylate solution furnishesd ethyl β-methylpentane-αβδ-tricarboxylate (II, $R_1=Me$; $R_2=H$; $X=Et$), which on cyclisation with sodium gives ethyl 2 : 4-dimethyl*cyclo* pentan-1-one 4 : 5-dicarboxylate (III, $R=H$; $R_1=Me$; $R_2=CO_2Et$; $X=Et$). This on hydrolysis with dilute acids affords 2 : 4-dimethyl*cyclo*pentan-1-one-4-carboxylic acid (III, $R=R_2=X=H$; $R_1=Me$) as a liquid, of which the semicarbazone melts at 173° alone or in admixture with an authentic specimen.

### *Synthesis of β-Methylpentane-αβδ-tricarboxylic Acid* (II,$R_1$=Me ; $R_2$=X=H) *and of 2 : 4-Dimethyl*cyclo*pentan-1-one-4-carboxylic Acid* (III, R=$R_2$=X=H ; $R_1$=Me).

Ethyl α-methyllaevulate (IV) has been condensed with ethyl cyanoacetate in presence of acetamide and acetic acid (Cope, *J. Amer. Chem. Soc.*, 1937, **59**, 2329) to give ethyl α-cyano-β-methyl-$\Delta^{\alpha}$-pentene-αδ dicarboxylate (V). This reacts with hydrogen cyanide with the formation of ethyl αβ-dicyano-β-methylpentane-αδ-dicarboxylate (VI) (*cf.*, Hope and Sheldon, *J. Chem. Soc.*, 1922, **121**, 2223 ; Lapworth and McRea, *ibid.*, p. 2752 ; Bardhan and Ganguly, *ibid.*, 1936, 1852). The latter on hydrolysis with concentrated hydrochloric acid affords (II, $R_1$=Me ; $R_2$=X=H), m.p. 178-79°. The ethyl ester (II, $R_1$=Me ; $R_2$=H; X=Et) on sodium condensation gives (III, R=H ; $R_1$=Me ; X=Et; $R_2$=$CO_2Et$), which on hydrolysis with ditute acids furnishes (III, R=$R_2$=X=H ; $R_1$=Me) which has been characterised by the formation of a semicarbazone, m.p., 173°.

$CO_2Et{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}Me$ (IV)

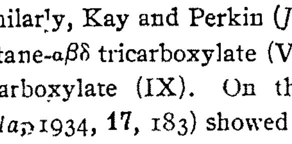
$CO_2Et{\cdot}CHMe{\cdot}CH_2{\cdot}CMe{:}C(CN{\cdot}CO_2Et$ (V)

$CO_2Et{\cdot}CHMe{\cdot}CH_2{\cdot}CMe(CN){\cdot}CH(CN){\cdot}CO_2Et$ (VI)

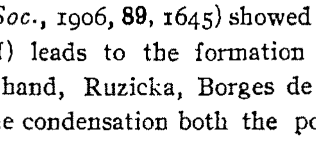
γ-Methylpentane-αγδ-tricarboxylic acid (II, $R_2$=Me ; $R_1$=X=H), which might have been formed by the hydrolysis of the keto-ester having the alternative structure (I), has already been described by Sen-Gupta (*J. Indian Chem. Soc.*, 1933, **10**, 343). The ester of this acid on cyclisation followed by hydrolysis in the usual way, however, furnishes a liquid keto-acid (III, R=X=$R_1$=H ; $R_2$=Me), the semicarbazone of which had m.p. 208° and thus differs markedly from the corresponding product derived from the isomeric keto-acid (III, R=X=H; $R_1$=Me ; $R_2$=H) described above.

It follows, therefore, that the action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate leads to the formation of ethyl 3-methyl*cyclo*pentan-1-one-3 : 5-dicarboxylate (III, $R_1$=$R_2$=H ; R= $CO_2Et$; X=Et) and not the isomeric ethyl 3-methyl*cyclo*pentan-1-one-2 : 3-dicarboxylate (III, R=$R_1$=H ; $R_2$=$CO_2Et$; X=Et),as suggested by Baker (*loc. cit.*).

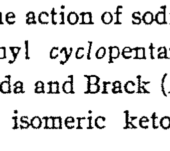
On searching the literature which has special reference to the Dieckmann condensation of analogously constituted tricarboxylic esters it is found that Perkin and Thorpe (*J. Chem. Soc.*, 1906, **89**, 781) isolated the keto-ester (VIII, R=Me) as the sole product of the condensation of ethyl ββ-dimethylbutane-αγδ-tricarboxylate (VII, R=Me) with sodium.



(VII)



(VIII)



(IX)

Similarly, Kay and Perkin (*J. Chem. Soc.*, 1906, **89**, 1645) showed that the action of sodium on ethyl butane-αβδ tricarboxylate (VII, R=H) leads to the formation of ethyl *cyclo*pentan-1-one-2 : 4-dicarboxylate (IX). On the other hand, Ruzicka, Borges de Almeida and Brack (*Helv. Chim. Acta*, 1934, **17**, 183) showed that in the condensation both the possible isomeric keto-esters (IX) and (VIII, R=H) are formed.

These experiments are significant from the point of view of the present investigation, as relatively small quantities of the keto-ester (III, R=$R_1$=H ; $R_2$=$CO_2Et$; X=Et) may also accompany the isomeric ester (III, $R_1=R_2=H$; $R=CO_2Et$; $X=Et$), which apparenty constitutes the sole product of the reaction. This must, however, remain an open question until further experiments, which are in hand, have been performed

## EXPERIMENTAL

Ethyl $\beta$-methylbutane-$\alpha\beta\delta$-tricarboxylate, required for this work, was prepared according to Ruzicka (*loc. cit.*), with a slight modification (*cf.* Sen-Gupta, *loc. cit.*), by condensing ethyl laevulate with ethyl bromoacetate in presence of zinc in benzene. The lactonic ester, thus obtained, was heated to 200-220° for 10 hours with $1\frac{1}{2}$ mol. of finely powdered potassium cyanide and the brown reaction product hydrolysed by heating on a sand-bath for 10 hours with excess of concentrated hydrochloric acid. The solution was then evaporated to dryness and the residue extracted with ether. The crude acid obtained on evaporation of the ether was esterified by the alcohol-vapour method when ethyl $\beta$-methylbutane-$\alpha\beta\delta$-tricarboxylate was obtained as a colourless mobile liquid, b. p. 142°/4mm.

*Sodium Condensation of Ethyl $\beta$-Methylbutane-$\alpha\beta\delta$-tricarboxylate and Methylation of the Sodio-salt: Formation of the Keto-ester* (III, $R=CO_2Et$; $R_1=Me$; $R_2=H$; $X=Et$).—Ethyl $\beta$-methylbutane-$\alpha\beta\delta$-tricarboxylate (36 g.) was heated on the water-bath with a suspension of finely divided sodium (3.5 g.) in dry benzene (90 c.c.). A vigorous evolution of hydrogen started on heating and the reaction was complete in 45 minutes. It was then cooled in ice and methyl iodide (12 c.c.) was added and kept over-night. The next day, it was refluxed for 16 hours with the addition of a little methyl iodide from time to time. The product was treated with water, the benzene layer was separated, washed and the benzene evaporated. The product obtained was then distilled as a colourless liquid, b. p. 135°/6 mm, yield 26 g. It gave no colouration with alcoholic ferric chloride. (Found: C, 60.6; H, 7.7. $C_{13}H_{20}O_5$ requires C, 60.9; H, 7.8 per cent).

*Acid Hydrolysis af the Methylated Product: Formation of $\beta$-Methylpentane-$\alpha\beta\delta$-tricarboxylic Acid* (II, $R_1=Me$; $R_2=H$; $X=H$).—The above product (10 g.) was heated on the water-bath for 3 hours with potassium hydroxide (10 g.) in 25% aqueous alcoholic solution. The alcohol was then evaporated off on the water-bath with the addition of water. It was then acidified and extracted with ether. The solid acid obtained on evaporation of the ether was crystallised from concentrated hydrochloric acid. The *pure* acid melted at 178-179° and there was no depression of the melting point when it was mixed with an authentic specimen. (Found: C, 49.2; H, 6.5. $C_9H_{14}O_6$ requires C, 49.5; H, 6.4 per cent).

*Formation of* (II, $R_1=Me$; $R_2=H$; $X=Et$) *from the Methylated Keto-ester* (III, $R=CO_2Et$; $R_1=Me$; $R_2=H$; $X=Et$).—The methylated keto-dicarboxylic ester (15 g.) was refluxed on the water-bath for 4 hours with a solution of sodium (0.35 g.) in absolute alcohol (16 c.c.). It was treated with water, acidified and extracted with ether, and the residual oil obtained on evaporation of the ether was distilled in *vacuo*, when with the exception of a little low boiling product (1.4 g), it boiled constantly at 140-42°/5 mm., yield 14.3 g.

*Cyclisation of the Triethylester obtained above: Formation of* (III, $R=H$; $R_1=Me$; $R_2=CO_2Et$; $X=Et$).—The above ester was heated on the water-bath with a suspension of molecular sodium (1.3 g.) in dry benzene (35 c.c.). The reaction started after heating for 10 minutes and was complete in an hour. The product was treated with water, acidified with ice-cold dilute hydrochloric acid and the benzene layer separated. The benzene solution was washed with water and the benzene evaporated. The product was then distilled at 130-33°/6mm. yield 9.3 g. It gives a strong colouration with alcoholic ferric chloride. (Found : C, 60.4 ; H, 7.8. $C_{13}H_{20}O_5$ requires C, 60.9 ; H, 7.8 per cent).

*Hydrolysis of the above Keto-ester to 2:4-Dimethylcyclopentan-1-one-4-carboxylic Acid* (III, $R_1=R_2=X=H$ ; $R=Me$).—The above ester (9 g.) was heated on a sand-bath for 6 hours with 10 volumes of 6% hydrochloric acid. The clear solution was neutralised with sodium carbonate and extracted with ether to remove any neutral matter. It was then acidified, saturated with salt and extracted with ether. The liquid keto-acid obtained on evaporation of the ether was converted into the *semicarbazone*. The semicarbazone melted at 173° (decomp.) after two crystallisations from methyl alcohol, and there was no depression of the melting point on mixing it with an authentic sample. (Found : C, 50.4 ; H, 7.0. $C_9H_{15}O_3N_3$ requires C, 50.7 ; H, 7.0 per cent).

*Synthesis of β-Methylpentane-αβδ-tricarboxylic Acid* (II, $R_1=Me$; $R_2=X=H$) *and 2:4-Dimethylcyclopentan-1-one-4-carboxylic Acid* (III, $R_1=Me$ ; $R_2=X=R=H$)

*Ethyl α-acetyl-β-methylsuccinate*.—Ethyl aceto-acetate (32.5 g.) was added dropwise to an ice-cold suspension of finely divided sodium (5.75 g.) in benzene (65 c.c.) and the solution kept over-night. It was then treated with ethyl α-bromopropionate (45·5 g.) and heated on the water-bath for 20 hours and worked up in the usual way, b.p. 120°/5mm., yield 37g.

*Ethyl α-Methyllaevulate* (IV) —The above product was hydrolysed by heating on a sand-bath for 8 hours with 5 volumes of dilute hydrochloric acid (1:2). The clear solution obtained was then evaporated to dryness. The dry residue (17 g.) was esterified by refluxing for 10 hours with absolute alcohol (80 c.c.) and 8 c.c. of alcoholic hydrogen chloride (saturated at 0°). The alcohol was then distilled off and the residue taken up in ether, washed with water, dried over calcium chloride, and the solvent evaporated. The residue was then distilled at 85°/7mm., yield 16 g.

*Ethyl α-Cyano-β-methyl-$\Delta^{\alpha}$-pentene-αδ-dicarboxylate* (V).—α-Methyl laevulic ester (15.2 g.), ethyl cyanoacetate (11.3 g.), acetamide (2 g.) and glacial acetic acid (30 c.c.) were taken in a flask provided with a short fractionating column. The acetic acid was distilled off slowly during 4-5 hours, so that the temperature of the vapour was always between 105° and 115°. It was then taken up in ether, washed well with water and the ether was evaporated. The residual liquid on distillation gave 14.5 g. of the unsaturated cyanoester, b.p. 148°/5mm. (Found : C, 61.5 ; H, 7.4. $C_{13}H_{19}O_4N$ requires C, 61.6 ; H, 7.5 per cent).

*Ethyl αβ-Dicyano-β-methylpentane-αδ-dicarboxylate* (VI).—The unsaturated cyano-ester (14.1g.) was dissolved in spirit (68 c.c.) and treated with a solution of potassium cyanide (7.2 g.) in water (39 c.c.). The warm product was then cooled in ice-water, treated, drop by drop, with 15·2 c.c. of 20% hydrochloric acid, and kept for 45 minutes. The product was diluted with a large volume of water and acidified with hydrochloric acid. The oil separating was extracted with ether and washed with water. The oily liquid, obtained on distillation of the solvent, was distilled at 176°/5 mm., yield 13.5 g. (Found : C, 59.7 ; H, 7.1. $C_{14}H_{20}O_4N_2$ requires C, 60.0 ; H, 7.1 per cent).

*β-Methyl pentane-αβδ-tricarboxylic Acid* (II, $R_1=Me$ ; $R_2=X=H$) was prepared from the dicyano ester (13.3 g.) by heating on a sand-bath for 12 hours with concentrated hydrochloric acid (75 c.c.). The clear solution obtained was evaporated to dryness on the water-bath and the solid residue was extracted with ether. On evaporation of the solvent the product solidified. The dry residue (10 g.) was esterified by dissolving in absolute alcohol (25 c.c.) and concentrated sulphuric acid (2.5 c.c.) and heating for 6 hours at 210° in a current of hot alcohol vapour. The product was then worked up and distilled at 140°/4 mm., yield 10 g. (Found: C, 59.4; H, 8.6. $C_{15}H_{26}O_6$ requires C, 59.6; H, 8.6 per cent).

The ethyl ester (1.5 g.) was heated on a sand-bath with 10 c.c. of concentrated hydrochloric acid till a clear solution was obtained. It was then evaporated to dryness. The acid (II, $R_1$=Me; $R_2$=X=H) was obtained on crystallisation of the residue several times from concentrated hydrochloric acid, m.p. 178-9°. It is readily soluble in water and hot concentrated hydrochloric acid but sparingly soluble in ether and cold concentrated hydrochloric acid. (Found: C, 49 4; H, 6.5. $C_9H_{14}O_6$ requires C, 49.5; H, 6.4 per cent).

The p-*phenylphenacyl ester* crystallises from a mixture of benzene and absolute alcohol, m p. 158°. (Found: C, 76.4; H, 5.6. $C_{51}H_{44}O_9$ requires C, 76.5; H, 5.5 per cent).

*Ethyl 2 : 4-Dimethyl*cyclo*pentan-1-one-4 : 5-dicarboxylate* (III, R=H; $R_1$=Me; $R_2$=$CO_2Et$; X=Et).—The triethyl ester (7.9 g.) was heated on a water-bath with a fine suspension of sodium (0.72 g.) in dry benzene (20 c.c.). The reaction started after 10 minutes and was complete in 45 minutes. It was treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The upper benzene layer was separated, washed well with water and the benzene distilled completely under reduced pressure. The product boiled at 126°/4mm., yield 4.5 g. It gives a violet colouration with alcoholic ferric chloride. (Found: C, 60.7; H, 7.6. $C_{13}H_{20}O_5$ requires C, 60.9; H, 7.6 per cent).

2:4-*Dimethyl*cyclo*pentan-1-one-4-carboxylic Acid* (III, $R_1$=$R_2$=X=H; R=Me).—The above product (4.2 g.) was heated on a sand-bath for 6-7 hours with 50 c.c. of 6% hydrochloric acid. The clear solution was neutralised with sodium carbonate and extracted with ether to remove any neutral matter. The aqueous solution was then acidified, saturated with salt and extracted with ether. The acid (III, $R_1$=$R_2$=X=H; R=Me) (2.3 g.) was obtained as a liquid on evaporation of the ether. The *semicarbazone* crystallises from methyl alcohol, m.p. 173° (decomp.). (Found: C, 50.4; H, 7.0. $C_9H_{15}O_3N_3$ requires C, 50.7; H, 7.0 per cent).

Further work is in progress.

My best thanks are due to Dr. J. C. Bardhan for his kind advice and criticism.

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# LATEX OF SOME INDIGENOUS RUBBER YIELDING PLANTS.
# PART I. *EXCAECARIA AGALLOCHA*, LINN

By S. V. Puntambekar and S. Krishna

The latex of *Excaecaria agallocha* has been shown to contain a fat, resin esters; resenes, rubber proteins, crude fibre and inorganic matter. The fat consists of the glycerides of lignoceric, cerotic, oleic and linoleic acids

Due to the present shortage of rubber in India an urgency has arisen to discover additional sources of this vital product necessitating the investigation of plant latices which may prove alternatives to *Hevea* rubber. In other countries similar attempts have been made, with the result that United States of America has started the cultivation of *Parthenium argentatum* (the Mexican plant Guayule, with 20% of rubber content. *Anon.*, 1942, *Chronica Botanica,* 7, (3) 138) and the United States of Soviet Russia is obtaining her demand of rubber from a species of dandelion (*Taraxacum tau-saghyz*), which is reported to be grown extensively in South Uzbekistan. In Australia intensive efforts are being made to extend the cultivation of the naturalized vine *Cryptostegia grandiflora* whose latex has been found to yield rubber as high as 23% (unpublished data by one of the authors). Even though the yield of rubber from these plants is not as high as from *Hevea* their cultivation etc. is being encouraged with a view to making the country not wholly dependent on foreign supplies.

No serious attempt appears to have been made in India to properly investigate the latices of indigenous plants which occur all over the country. Some of these, especially those belonging to the families, *Apocynaceae, Asclepiadaceae, Euphorbiaceae, Compositae* and *Urticaceae,* yield latices which contain rubber. Any of these may turn out to be a rich source of rubber but unfortunately the information on the yield of latex and its rubber content is not available. It is for this reason that the present investigation has been started and it is proposed to examine only those plants which are known to occur in abundance. One such plant is *Excaecaria agallocha* which covers nearly 400 sq. miles in Sundarbans and of which nearly 300,000 trees per annum could be made available for the tapping of latex.

Genrally speaking, latices contain resin and caoutchouc and that latices from different species of trees are different in character even in closely related species. Some contain high proportion of caoutchouc and lower proportion of resin and proteins, whilst the majority contain higher proportion of resin which are intimately associated with caoutchouc, yielding rubber of poorer quality. Those with a high proportion or resin or resin like substances are, in normal times, of small value for rubber although they may be useful for other purposes. From the commercial point of view, however, this association with high proportion of resin is undesirable and unsuitable for the extraction of rubber. *Hevea* latex, for example, contains obout 36·0% of caoutchouc, 2·0% resin and 2·0% of proteins, whereas the latex from *Calotropis procera* contains about 2·0% rubber, and 20 per cent. of resin and proteins, making it unsuitable as the source of rubber. In the present emergency, however, any latex that contains a reasonable amount of rubber is of value and should be investigated.

*Hevea*, as it is known to-day, is the result of intensive cultural operations and developments and should not therefore be taken as standard for its rubber content when comparing the plants which grow in wild state. It is possible to improve the rubber content of wild plants also, with cultivation and selection of proper strains. This, however, is a long term research and not likely to yield results of value during the present urgency, but the same urgency demands that all possible sources should be examined even though the rubber content may not be as high as in *Hevea*.

*Excaecaria agallocha*, Linn., Vern. *gewa* (Bengal), is a small evergreen bushy tree of the coastal and tidal forests. It is very common in Sundarbans and also occurs in the deltas of the Godavari and the Kistna. When a sharp cut is made on its bark a quantity of an acrid milky juice flows down which on drying hardens to a black caoutchouc-like material. One set of cuts gives milk for only a minute or two and then a fresh cut has to be made when again the juice flows copiously and ceases after a couple of minutes.

The latex was obtained through the courtesy of the Divisional Forest Officer, Sundarbans, who had sent the material in sealed tins without the addition of ammonia. The chemical examination showed it to contain only 2·7% of rubber, which quantity is obviously too low for commercial extraction. The results of the chemical examination of this latex do not appear to have been recorded before and are, therefore, being reported now. The method adopted for the separation and isolation of the various constituents of this latex is in general the same as recommended for para rubber latex (Davis and Sadtler, Allen's Commercial Organic Analysis, 4th Ed. Vol. 4, p. 106). It had, however, to be modified in the present case to separate the fatty oil and resin esters from the resenes occuring in the latex.

## EXPERIMENTAL

The latex had the following characteristics :—

| | | | | | |
|---|---|---|---|---|---|
| Colour | Light yellow | Odour | repulsive | Specific gravity at 28° | 0·9723 |
| Acid value | 4 0 | Steam volatile matter | nil | Water solubles | 4·0% |
| Coagulated mattter | 34·0% | Total solids | 38·0% | Ash | 1·7% |

500 G. of the latex were diluted with water to a litre and coagulated with the addition of 5 c.c. of glacial acetic acid at 80°. The precipitate was allowed to settle and the supernatant liquid decanted. The residue was stirred with hot water, the solids again allowed to settle and the supernatant liquid decanted. This operation was repeated a few times after which the thick slurry of the coagulated matter was centrifuged to remove most of the water. It was than dried at 105°C. The yield of the dried coagulated solids was 170 g. The nature of the water solubles has not been investigated but qualitative tests showed it to contain reducing sugars and no starch.

*Fat and resin.*—The dried coagulated solids were extracted twice with acetone, under reflux, for 5 hours, the extract cooled and the solids filtered off. On distilling off acetone 100 g. of a transparent, balsam like, reddish brown, viscous fluid (acid value 2, saponification value 41·2) was obtained. Preliminary examination showed this to be a mixture of a fat and resins. Consequently the method as described below was adopted to effect their separation :—

*Fat.*—The viscous fluid (100 g.) was saponified with alcoholic sodium hydroxide as in the case of a fat. After the removal of alcohol by distillation, the saponified mass was taken up in hot water and the soapy solution was decomposed with concentrated hydrochloric acid to precipitate the mixed fatty acids and the resin acids along with neutral resins and unsaponifiable matter. These were removed while hot through a separating funnel and washed with hot water. The separated acid mother liquor and washings were made just alkaline and evaporated to dryness. The residue showed the presence of glycerol.

The mixture of the separated fatty acids, resin acids, neutral resins and unsaponifiable matter was neutralised with 25% sodium hydroxide, the resulting soap solution was incorporated with washed filter-paper pulp and the whole mass thoroughly dried. It was then extracted with ethyl ether, in a soxhlet, to remove the unsaponifiables *i.e.*, all the resenes and the small amount of unsaponifiable matter. The residual soap was dissolved in water, the filter paper thoroughly squeezed and the total acids liberated with strong hydrochloric acid. These were washed, dried and filtered, the yield being 41 g. They were then separated into (*a*) solid acids, 6·7 g. (16·3%), (*b*) liquid acids, 31·4 g. (76·7%, Iodine value 92·5) and (c) resin acids 2·9 g. (7%) by Twitchell's method (Twitchell, *Ind. Eng. Chem.*, 1921, **13**, 806).

(*a*) The solid acids were fractionally crystallised from 95% alcohol. Two sets of fatty acid crystals were obtained, one melting at 80-81° (M. W. 369) and the other at 87°-88° (M.W. 400). These appeared to be lignoceric and cerotic acids, but were confirmed by their mixed melting points with pure lignoceric acid and pure cerotic acid respectively.

(*b*) The liquid acids whem brominated in cold ether, according to the method of Eibner and Muggenthaler (Lewkowitsch and Warburton, *Chemical Technology and Analysis of Oils, Fat and Waxes*, 1921, 6th Ed., Vol. I; 585) gave no precipitate of a hexabromide. The residue after evaporation of ether and crystallisation from petroleum ether yielded some crystals (m.p. 113°-114°) of linoleic tetrabromide. Isolation of this compound and the iodine value of the liquid acids show that they consist of oleic and linoleic acids.

(*c*) The resin acids were obtained in the form of their lead salts insoluble in boiling alcohol, in the Twitchell's separation. After decantation of the hot alcoholic solution of the salts of solid and liquid acids they were obtained by treating the residue with hot dilute hydrochloric acid. They were presumably derived from resin esters, associated with the fat and resin of the acetone extract.

*Resin*:—The ethereal solution of the unsaponifiables on distilling oft the ether, yielded a brownish red, transparent, neutral resin (57 g.). It melted at 52°-54° and dissolved in almost all the organic solvents including petroleum ether. Its iodine value was 90·0. When distilled over sodium hydroxide at 200-250° it splits up into an aromatic distillate, $[n]_D^{30°}$, 1·5103, and an acidic residue. None of these were further investigated.

*Rubber.*—The acetone insoluble portion (70 g.) was refluxed twice with 150 c.c. of chloroform for 2 hours and filtered. After distilling off chloroform from the filtrate the residue weighed 13·40 g. This was caoutchouc.

*Protein, fibre etc*—The chloroform insoluble portion (56·6 g.) was a pink amorphous substance (acid value 10·4), insoluble in organic solvents. Salt solution dissolved a portion of it. Its nitrogen content was 11·2%. The major portion of the substance thus appeared to be protein and on the basis of its nitrogen content it contained 70% of proteinous matter and the balance 30% was crude fibre and inorganic matter. Being of no interest none of these products were investigated further.

*Composition of the latex.*—On the basis of the above data the chemical composition of the latex works out as follows:—

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Water | 62·0% | Water solubles | 4·0% | Ash | 1·7% | Fibre | 1·7% |
| Proteins | 7·9% | Fat and resin esters | 8 6% | Resenes | 11·4% | Rubber | 2·7% |

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# A NOTE ON THE ALKALOID IN *ECLIPTA ALBA* (HASSK)

By S. N. Pal and M. Narasimham

Dymock and his co-workers (*Pharmacographia Indica*, Vol. II., p. 268) mention that "an alkaloidal principle was detected in *Eclipta alba* which we failed to obtain in a crystalline form. It afforded no special colour reactions. The sulphate was slightly soluble in ether" The investigation of the present workers confirms the existence of an alkaloid in the plant. This alkaloid is volatile with steam and has been identified as nicotine. As no other alkaloid could be detected, it is suggested that ecliptine is identical with nicotine.

## EXPERIMENTAL

*Isolation of the Alkaloid.*—In a preliminary examination, 100 g. of the dry plant were kept immersed in Prollius' fluid for 12 hours and filtered. The filtrate was concentrated and tested with the reagents for the alkaloids with positive results. For isolating the alkaloid, 4 kg. of air-dried plant were treated in 4 lots of 1 kg. each. Each lot was kept immersed in 1% hydrochloric acid for 12 hours and then filtered. No alkaloid could be detected in the residue. 40 G. of sodium hydroxide were added to the filtrate and the solution was subjected to steam distillation. The distillation was stopped as soon as the distillate ceased to give pink colour with phenolphthalein. In this way, 300 c.c. of aqueous distillate from each lot were collected. The solution remaining in the flasks was evaporated to dryness on a water-bath. A black amorphous mass containing carbon, hydrogen, nitrogen, sulphur and phosphorus was obtained. This might be the 'resin' mentioned by Dymock and his co-workers and this on examination did not show the presence of an alkaloid. The aqueous distillates from each lot were mixed together and shaken repeatedly with equal volumes of ether in a separating funnel. All ethereal extracts were collected and ether distilled off at 30°/177 mm. A colourless liquid (3·1 g.) remained. This began to turn brown giving tobacco odour. It responds to all the tests for nicotine. It was immediately re-distilled in hydrogen, b.p. 247°. (Found: C, 73·1, H, 8·6; N, 17·25. Calc. for $C_{10}H_{14}N_2$ . C, 74·06; H, 8·64; N, 17·3 per cent).

*Preparation of the Oxalate.*—The alkaloid (5 g.) was dissolved in ether (50 c.c.) and treated with an ethereal solution (50 c.c.) of calculated quantity of oxalic acid and the solution shaken well. Ether was distilled off under reduced pressure. Colourless crystals remained, m.p. 77°, becoming 109° after resolidifying.

*Preparation of Nicotinic Acid.*—The alkaloid (0·5 g.) was mixed with dilute nitric acid (50 c.c.) in a dish and then evaporated to dryness on a water-bath, A brown solid remained, m.p. 228°. (Found: C, 57·2; H, 4·1; N, 11·1. Calc. for $C_5H_4NCOOH$ : C, 58·5; H, 4·06; N, 11·3 per cent).

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# SUPERSATURATION LIMITS OF SOLUTIONS. PART I

BY RAMA GOPAL

It is shown that aqueous solutions of some salts, saturated at temperature $T_S$, when cooled uniformly in a thin-walled sealed glass tube, crystallise at almost a fixed temperature $T$. Further, $T_S - T$ is found to be approximately constant for the same solute irrespective of the value of $T_S$ within the temperature range studied herein. Again for some of the salts investigated the molecular heat of solution, $\lambda$ appears to vary inversely as $T_S - T$, *i.e.*, $(T_S - T)\ \lambda =$ a constant (approx.). A theoretical deduction of this relationship, based on the theory of supersaturation of Jones and Partington has been advanced.

In some cases, $T_S - T$ has, however, been found to increase rapidly with successive heating and cooling. The difference between the behaviours of these two types of salts is noted without suggesting any hypothesis to explain this difference.

A third type of substances has been observed to show no spontaneous crystallisation even after considerable cooling. Behaviours of the first and the third type of substances have been discussed.

A survey of literature reveals that no serious attempt has been made to study the relative supersaturation of various substances in any given solvent and its dependence on any property of the entities concerned. Jones (*J. Chem. Soc.*, 1908, **93**, 1739) pointed out that relative supersaturation of $KNO_3$, $RbNO_3$ and $CsNO_3$ varied inversely as their molecular weight, and probably, directly as their hydration. Jones and Partington (*Phil. Mag.*, 1915, **29**, 35; *J. Chem. Soc.*, 1915, **107**, 1019) emphasised the importance of the surface energy of the solute in the phenomenon of supersaturation. But apart from a few more investigations of more or less qualitative nature no other significant work is available. It is, therefore, desirable to study various substances from the point of view of their relative supersaturation in the commonest solvent water to start with.

From the researches of Berkley (*Phil. Mag.*, 1912, **24**, 254), Young and his collaborators (*J. Amer. Chem. Soc.*, 1911, **33**, 148, 1375; 1913, **35**, 1065) and others it appears that spontaneous crystallisation in a solution or melt is to a very great extent dependent on the mechanical shock to which it is subjected as well as on the number and nature of the insoluble nuclei present. It is, therefore, essential that all experiments must be performed under comparable conditions to get the relative values of supersaturation. Also from these works it is definitely established that the *metastable range*, in Ostwald's terminology, may not be a very suitable expression to denote the region of relative supersaturation as solutions in this region have been supposed to be quite immune to crystallisation under all circumstances except the addition of nuclei from without. For this reason it is preferably called here *the supersaturation limit* to denote the difference between the saturation temperature $T_S$ and that of spontaneous crystallisation $T$ (both in degrees centigrade) when a solution in a thin-walled sealed glass tube cools uniformly at rest.

## EXPERIMENTAL

Required amounts of water and chemicals (necessary for saturation at any temperature $T_S$) recrystallised from conductivity water and protected from dust as far as possible, were sealed in well steamed and dried similar thin-walled glass tubes. Generally 4 g. of water were used. The sealed tube was attached to a stout glass tubing with rubber bands and placed in a beaker (800 to 1000 c.c. capacity) containing water enough to keep it wholly immersed. The beaker was heated to a temperature approximately 10° higher than $T_S$ of the solution in the tube. By repeated shakings the solute was dissolved in the minimum possible time. The beaker was then allowed to cool slowly, keeping the sealed tube completely at rest, the temperature of the beaker falling by 1° in about 5 to 10 minutes. It was arranged with the help of a microburner placed under the beaker. This device assures that the temperature inside the sealed tube is the same as that of the outer bath. Some control experiments with similar tubes carrying 4 g. of water, and a thermometer dipped in it, and closed at the mouth with a cork, were performed in the above bath which cooled unaided by a microburner. It has been found that when temperature falls 1° in about 5 minutes, the temperatures inside the closed tube and outside in the beaker are the same.

The temperature $T$ of the bath, at which spontaneous crystallisation in the sealed tube started was noted. Observations were made with the help of a pocket lens. The above process of heating and cooling was repeated three times or more and observations made as before. Thermometers used were graduated in 1/5° and were standardised against a thermometer with National Physical Laboratory certificate. Solubilities used were as recent as possible. Graphs were plotted from available figures in case where solubilities were not given at proper interval of temperatures and from these graphs required solubilities were read off. But older values from Comey and Hahn's "Dictionary of Chemical Solubilies etc," were employed where recent works failed to show any marked difference. The results thus obtained are given in the following tables.

In a number of other aqueous solutions like those of $SnCl_2$, $HIO_3$, $ZnCl_2$, $CH_3COONa$, $CdSO_4$, $Na_2S_2O_8$ etc. it has not been possible to get any temperature of spontaneous crystallisation within the range of temperatures investigated.

From the tables it is clear that in some cases the temperature $T$ remains almost constant after repeated heatings and coolings whereas in others it varies with the number of heatings. $T_s - T$, in general, is obtained with the first temperature of spontaneous crystallisation as in this

TABLE I

| KCl | | | | | KBr | | | | | KI | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_s$. | $T$ | | | $T_s - T$. | $T_s$. | $T$ | | | $T_s - T$. | $T_s$. | $T$ | | | $T_s - T$. |
| 40 | 21·0 | 21·0 | 21·6 | 19·0 | 37 | 20·0 | 20·2 | 20·0 | 17·0 | 35 | 20·0 | 20·2 | 20·0 | 15·0 |
| 45 | 26·0 | 26·5 | 25·8 | 19·0 | 42 | 25·2 | 25·0 | 25·4 | 16·8 | 40 | 24·6 | 25·0 | 23·6 | 15·4 |
| 50 | 30·4 | 30·2 | 30·0 | 19·6 | 45 | 28·6 | 28·5 | 28·0 | 16·4 | 45 | 29·4 | 29·8 | 29·6 | 15·6 |
| 55 | 38·6 | 38·5 | 37·4 | 16·4 | 50 | 34·0 | 34·5 | 33·8 | 16 0 | 50 | 34·2 | 35·0 | 34·4 | 15·8 |
| 60 | 42·8 | 42·0 | 40·4 | 17·2 | 55 | 38·4 | 38·5 | 38·0 | 16·0 | 55 | 45·0 | 39·6 | 39·4 | 15·4 |
| 65 | 45·8 | 46·0 | 45·6 | 19·2 | 58 | 41·4 | 40·6 | 42·2 | 16·6 | 60 | 44·8 | 44·2 | 44·2 | 15·2 |
| 70 | 49·6 | 47·4 | 43·0 | 20·4 | 65 | 49·2 | 48·8 | 48·4 | 15·8 | 65 | 49·6 | 50·2 | 49·5 | 15 4 |
| 75 | 54·4 | 48·4 | 54·0 | 20·6 | 70 | 52·8 | 53·4 | 52·8 | 17·2 | 70 | 54·6 | — | — | 15·4 |
| 80 | 59·8 | 59·6 | 52·8 | 20·2 | 75 | 55·8 | 57 4 | 58·8 | 16·2 | 77 | 61·8 | 62·6 | 61·6 | 15·2 |
| | | | | | 80 | 62·6 | 62·6 | 62·4 | 17·4 | 80 | 64·6 | 64·2 | 64·0 | 15·4 |
| | | | Mean | 19·5 | | | | Mean | 16·3 | | | | Mean | 15·5 |

TABLE I (*contd.*)

$KClO_3$

| $T_S$. | $T$. | | | $T_S - T$. |
|---|---|---|---|---|
| 30 | 24·0 | 23·6 | 23·0 | 6·0 |
| 37 | 30·6 | 30·5 | 30·0 | 6·4 |
| 40 | 33·4 | 33·5 | 32·0 | 6·6 |
| 45 | 39·0 | 39·0 | 38·4 | 6·0 |
| 50 | 43·4 | 43·5 | 43·0 | 6·6 |
| 55 | 47·8 | 47·4 | 47·2 | 7·2 |
| 60 | 53·4 | 53·0 | 53·6 | 6·6 |
| 62·5 | 56·0 | 55·8 | 52·6 | 6·5 |
| 65 | 57·4 | 56·6 | 56·6 | 7·6 |
| 70 | 63·0 | 63·6 | 62·9 | 7·0 |
| | | | Mean | 6·6 |

$KClO_4$

| $T_S$. | $T$. | | | $T_S - T$. |
|---|---|---|---|---|
| 30 | 23·6 | 24·0 | 23·5 | 6·4 |
| 33 | 27·0 | 27·2 | 27·5 | 6·0 |
| 35 | 28·4 | 28·0 | 27·6 | 6·6 |
| 40 | 33·8 | 33·5 | 33·5 | 6·2 |
| 45 | 39·0 | 38·9 | 38·8 | 6·0 |
| 50 | 43·5 | 43·7 | 43·7 | 6·5 |
| 52·5 | 46·8 | 47·0 | 46·0 | 5·7 |
| 55 | 48·6 | 48·0 | 48·4 | 6·4 |
| 60 | 53·4 | 53·4 | 53·4 | 6·6 |
| 65 | 58·1 | 57·6 | 57·4 | 6·7 |
| | | | Mean | 6·3 |

$KBrO_3$

| $T_S$. | $T$. | | | $T_S - T$. |
|---|---|---|---|---|
| 35 | 26·0 | 25·4 | 21·0 | 9·0 |
| 40 | 31·5 | 31·0 | 31·0, 30·0 | 8·5 |
| 45 | 36·0 | 35·4 | 34·6 | 9·0 |
| 48 | 39·0 | 36·4 | 37·2 | 9·0 |
| 50 | 40·6 | 40·0 | 38·2 | 9·4 |
| 55 | 46·8 | 46·2 | 39·2 | 8·2 |
| 60 | 51·0 | 51·2 | 50·6 | 9·0 |
| 68 | 60·6 | 60·5 | 59·6 | 7·4 |
| 70 | 61·6 | 61·6 | 62·0 | 8·4 |
| 75 | 65·8 | 65·2 | 63·8 | 9·2 |
| | | | Mean | 8·8 |

$KNO_3$

| $T_S$. | $T$. | | | $T_S - T$. |
|---|---|---|---|---|
| 35 | 22·8 | 21·5 | 21·5 | 12·2 |
| 40 | 25·8 | 25·5 | 26·0 | 14·2 |
| 45 | 31·5 | 32·0 | 31·7 | 13·5 |
| 50 | 37·0 | 37·0 | 36·2 | 13·0 |
| 55 | 42·0 | 42·0 | 41·2 | 13·0 |
| 60 | 46·6 | 46·4 | 46·8 | 13·4 |
| 65 | 52·6 | 52·2 | 52·4 | 12·4 |
| 70 | 56·6 | 56·8 | 56·6 | 13·4 |
| 75 | 62·6 | 61·6 | 62·6 | 12·4 |
| 80 | 66·9 | 66·6 | 66·8 | 13·2 |
| | | | Mean | 13·0 |

$KIO_3$

| $T_S$. | $T$. | | | $T_S - T$. |
|---|---|---|---|---|
| 35 | — | 24* | — | — |
| 40 | 29·0 | 27* | — | 11·0 |
| 45 | 30·6 | 27* | — | 14·5 |
| 50 | 35·8 | 33·4 | 30·0 | 14·2 |
| 55 | 40·6 | 38·6 | 37·6 | 14·4 |
| 60 | 47·2 | 47·0 | 43·4 | 12·8 |
| 65 | 51·0 | 47·2 | 42·6 | 14·0 |
| 70 | 55·9 | 52·2 | 52·0 | 14·1 |
| 75 | 61·6 | 60·6 | 56·5 | 13·4 |
| 80 | 67·0 | 67·0 | 65·6 | 13·0 |
| | | | Mean | 13·5 |

$NaNO_3$

| $T_S$. | $T$. | | | $T_S - T$. |
|---|---|---|---|---|
| 40 | 26·0 | 26·5 | 26·2 | 14·0 |
| 43 | 29·0 | 28·6 | 28·0 | 14·0 |
| 45 | 32·0 | 32·4 | 32·0 | 13·0 |
| 50 | 38·0 | 38·2 | 40·0 | 12·0 |
| 55 | 42·1 | 41·4 | 41·4 | 12·9 |
| 58 | 45·2 | 45·1 | 45·4 | 12·8 |
| 60 | 47·2 | 47·0 | 46·8 | 12·8 |
| 65 | 51·2 | 51·6 | 51·2 | 13·8 |
| 70 | 57·6 | 57·9 | 58·0 | 12·4 |
| 75 | 61·4 | 61·2 | 61·6 | 13·6 |
| | | | Mean | 13·0 |

* Solutions did not crystallise down to these temperatures.

TABLE II

| Substance | $T_S$. | $T$. | | | | | $T_S - T$. |
|---|---|---|---|---|---|---|---|
| $Ba(NO_3)_2$ | 50 | | 32·0 | 28·2 | 26·2 | | 18·0 |
| | 55 | | 36·4 | 33·2 | 25·4 | | 18·6 |
| | 60 | | 41·2 | 37·0 | 28·4 | | 18·8 |
| | 65 | | 46·2 | 47·4 | 37·0 | | 18·8 |
| | 70 | | 51·4 | 44·2 | 31·8 | | 18·6 |
| | 75 | | 57·5 | 56·8 | 46·2 | 42·0 | 17·5 |
| $NH_4Cl$ | 55 | 35·0 | 28·2 | 24·4 | 26·0 | 21·5 | 20·0 |
| | 60 | 38·2 | 30·0 | 35·1 | 31·1 | 26·0 | 21·8 |
| | 65 | 52·4 | 42·2 | 28·0 | 27·2 | 28·0 | 12·6 |
| $(NH_4)_2SO_4$ | 55 | 34·0 | 29·6 | 26·4 | 25·0 | | 21·0 |
| | 60 | 36·5 | 34·0 | 25·4 | 24·2 | | 23·5 |
| | 65 | 41·2 | 39·4 | 30·2 | 29·6 | | 23·8 |
| | 70 | 45·2 | 40·0 | 31·0 | 30·8 | | 24·8 |
| | 80 | 55·4 | 50·2 | 35·0 | 34·5 | | 24·6 |

| Substance | $T_S$. | $T$. | | | | | $T_S - T$. |
|---|---|---|---|---|---|---|---|
| Oxalic acid | 50 | 35·0 | 30·2 | 31·4 | 28·2 | 28·2 | 15·0 |
| | 55 | 40·8 | 36·0 | 33·2 | 34·0 | — | 14·2 |
| | 60 | 47·2 | 47·4 | 40·1 | 35·0 | 35·2 | 12·2 |
| | 65 | 51·0 | 48·3 | 45·6 | 44·2 | 45·0 | 14·0 |
| | 70 | 57·4 | 47·2 | 42·2 | 47·3 | 57·0 | 12·5 |
| Urea | 82 | 68·6 | 60·5 | 60·6 | 49·4 | 68·6 | 11·4 |
| | 70 | 57·4 | 57·8 | 45·2 | 44·0 | 38·2 | 12·6 |
| | 60 | 47·0 | 45·2 | 46·9 | 47·0 | 41·0 | 13·0 |
| | 50 | 35·6 | 25·0 | — | — | — | 14·4 |
| | 45 | 32·0 | 30·0 | 25·6 | 23·0 | — | 13·0 |
| Succinic acid | 55 | 35·4 | 32·0 | 28·2 | — | — | 19·6 |
| | 60 | 45·4 | 43·6 | 38·2 | 40·0 | 42·0 | 15·6 |
| | 65 | 44·3 | 42·5 | 39·0 | — | — | 20·8 |
| | 70 | 49·4 | 47·3 | 48·4 | 47·0 | 41·2 | 20·6 |
| | 74 | 53·4 | 54·6 | 55·6 | 45·2 | — | 19·6 |
| | 80 | 59·0 | 58·0 | 55·0 | 50·8 | 54·0 | 21·0 |

condition all the solutions may be expected to be in identical environments. It must not be assumed, however, that solutions would not crystallise above $T$ under any circumstances. Effects of mechanical stimulus and insoluble nuclei are well known (*loc. cit.*). Prolonged keeping above $T$ may bring about crystallisation as is clear from the researches of Jaffe (*Z. physikal. Chem.*, 1903, **43**, 565) and others. What is implied by $T$ is that this temperature appears to lie in the most favourable position on the temperature-energy diagrams obtained by Young (*loc. cit.*). The energy value corresponds to that of the shocks prevalent in a common laboratory room, *i.e.*, at this temperature the solution crystallises out under the influence of shocks prevalent in laboratory rooms within the time of experiments.

## DISCUSSION

Referring to monobasic salts of Na and K given above it appears that the molecular heat of solution $\lambda$ of the salts varies almost inversely as the corresponding $T_s - T$, *i.e.*, $\lambda(T_s - T)$ is approximately constant. This is clear from Table II.

The constancy of the expression $(T_s - T)\lambda$ follows from the equation of Jones and Partington (*loc. cit.*). This equation connects the absolute temperature $T$ and the radius $r$ of the solute particle which is in equilibrium with a solution saturated at $T$ (*i.e.* particles of smaller radii will dissolve but of greater ones will start spontaneous crystallisation at this temperature) in the relationship,

$$T = C(1 - 1/kr) \qquad \ldots \quad (i)$$

where $C$ is the integration constant and $k = \rho\lambda/2M\sigma$, the terms used have their usual significance. The equation (*i*) is applicable to solutions of substances with negative heat of solution and only the numerical values of $\lambda$ should be taken into account as the general expression $T = C\left(1 + \frac{1}{kr}\right)$ reduces to (*i*) when proper value of $\lambda$ is substituted. When $T$ equals the ordinary saturation temperature $T_s$, $r = \infty$. In this case $T_S = C$ ... ... ... ... (*ii*)

From (*i*) and (*ii*) we obtain
$$(T_s - T) = \frac{C}{kr} = T_s \Big/ \frac{\rho\lambda r}{2M\sigma} = \frac{2\sigma M}{\rho\lambda} \cdot \frac{T_s}{r}$$

or
$$\lambda(T_s - T) = \frac{2\sigma M}{\rho} \cdot \frac{T_s}{r} = 2\sigma V_m \cdot \frac{T_s}{r} \qquad \ldots \quad (iii)$$

where $V_m$ denotes the molecular volume. According to various workers (Jones and Partington, *loc. cit.*, de Coppet and Tammann, "Krystallisieren und Schemelzen," Leipzig, 1903, p. 148)

TABLE III

| Salt. | $-\lambda$. | $(T_s - T)$. | $-\lambda(T_s - T)$*. | Salt. | $-\lambda$. | $(T_s - T)$. | $-\lambda(T_s - T)$*. |
|---|---|---|---|---|---|---|---|
| KCl | 4046 | 19·5 | 78897 | $KClO_3$ | 9950 | 6·6 | 65670 |
| KBr | 5080 | 16·3 | 82804 | $KNO_3$† | 8800 | 13·0 | 114400 |
| KI | 5110 | 15·5 | 79205 | $KClO_4$ | 12100 | 6·3 | 76230 |
| $KBrO_3$ | 9760 | 8·8 | 84788 | $NaNO_3$ | 5030 | 13·0 | 65390 |
| $KIO_3$ | 6780 | 13·5 | 91490 | NaCl‡ | 1220 | 51·0 | 62220 |
|  |  |  |  |  |  |  | Mean 80000 (approx.) |

---

* As the values of $\lambda$ given here correspond to very dilute solutions, the relationship must be considered as highly approximate.

† An average value derived from the observations of Jaffe (*loc cit.*) is 13·8 as Table IV shows.

‡ It was difficult to observe the formation of crystals in this case due to an almost colourless nature of crystals and their slow growth. But it was observed $T_s - T$ to be about 50. This is, however, in close agreement with the value obtained by de Coppet (*Compt. rend.*, 1872, **74**, 328) according to whom it is about 47 to 51.

TABLE IV

| $KNO_3$ (in 100 g. of water). | $T_s$. | $T$. | $(T_s-T)$. | $KNO_3$ (in 100 g. of water). | $T_s$. | $T$. | $(T_s-T)$. |
|---|---|---|---|---|---|---|---|
| 45·0 g. | 30·5 | 17·5 | 13·0 | 58·6 g. | 37·3 | 22·8 | 14·5 |
| 51·8 | 33·8 | 19·4 | 14·4 | 62·9 | 39·4 | 26·2 | 13·5 |
| 53·4 | 34·8 | 20·0 | 14·2 | | | Mean | 13·8 |

$r$ varies as $T_s$, *i.e.*, $T_s/r$ is a constant. Further $r$ in the case of similar substances may be taken to be of the same order. So that

$$\lambda(T_s-T)\lambda_s \propto \sigma V_m$$

The researches of Jaeger* (*Z. anorg. Chem.*, 1917, **101**, 185) and Dundon (*J. Amer. Chem. Soc.*, 1923, **45**, 2665) show that $\sigma V_m$ is approximately constant for similar substances. Assuming that $\sigma V_m$ does not change much within the range of temperatures studied, it follows that

$$(T_s-T)\lambda = \text{a constant (approx.)}.$$

From the results arrived at above electrolytes can be roughly divided into three main classes. First types are those in which supersaturation is, in general, not very great and almost a constant $T_s-T$ is obtained at least in the first few heatings, *e.g.*, $KNO_3$, $KClO_4$, etc. or the variation in $T_s-T$ with number of heatings is small. Second type comprises those for which $T_s-T$ increases rapidly with repeated heatings, *e.g.*, $Ba(NO_3)_2$, $NH_4Cl$, etc. Jaffe (*loc. cit.*) has shown that $T_s-T$ can be increased even in the case of $KNO_3$ by intensive filtration of the solution although it may be seen from the observations that it does not appreciably change up to 5 to 6 operations in most cases. Similarly Issac (*J. Chem. Soc.*, 1908, **93**, 384) pointed out that in solutions of $x NaNO_3 : y Pb(NO_3)_2 : z H_2O$ mixtures when boiled from 18 to 30 hours, $T_s-T$ increases even when tubes are shaken while cooling. This is well explained on the assumption of the presence of dust nuclei which are gradually removed in the process of filtration or on continuous boiling. The effect of heating on supersaturation limits has been very exhaustively studied by a number of workers specially in the case of organic liquids and various theories have been put forward depending mainly on the assumption of the presence of crystalline nuclei which are gradually dissolved or broken up into less effective smaller fragments in the process of heating. These have been well summarised by Richards (*J. Amer. Chem. Soc.*, 1932, **54**, 479) and Richards, Kirkpatrick and Hutz (*ibid.*, 1936, **58**, 2243). It is very difficult to fit in these theories in the extreme case of the first type of above mentioned substances unless we assume that these are very sensitive to crystalline nuclei while the others are not so. It is premature to make any decision or suggest another hypothesis at the present stage. It is expected that further investigation might lead to some definite conclusion.

To the third category belong the substances which show no spontaneous crystallisation even on strong cooling, *e.g.*, $CH_3COONa$, $Na_2S_2O_3$, $HIO_3$, $SnCl_2$, $AlCl_3$, $ZnCl_2$, etc. (*cf.* Bhattacharya and Dhar, *Proc. Akad. Wetensch.*, 1915, **18**, 369; Seysenegg, *Mikrochem.*, 1939, **27**, 96). Great affinity of these substances for water molecules is supported by the researches of Jones, Biltz and their collaborators as well as by the recent work on the entropy of ions and their apparent ionic volumes in aqueous solution. It may be added that most of these substances have got a positive heat of solution in the anhydrous condition.

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* Only $\sigma$ of melts are given. It may be reasonably expected that for similar solutes, *i.e.*, solutes which behave similarly towards the solvent (water) the variations, if at all, will also be similar though they may not be exactly identical.

It may now be visualised how in the case of type III salts a very high supersaturation is obtained. On dissolution a very compact sheath of water molecules is formed round the ions and molecules of the solute as the affinity between them is very high, whereas a very weak binding, if at all, occurs with substances of the first type. Hence the formation of stable nuclei is easier in the case of substances of type I but difficult in those of type III as the lattice forming units will hardly have any chance of coming together during the normal course of time. Moreover, it will be easier for the entities in the former type to smash through weak covering of water molecules around them and join hands with their opposite number when their affinity under these circumstances overcomes the effect of the outer sheath but it will be difficult and highly improbable in the case of substances of type III due to compact nature of the outer coverings. Besides, the high viscosity of the aqueous solutions of these substances, which is most probably due to their great affinity for water molecules, hinders the free movement of the lattice-forming units the probability of whose coming together is, therefore, further reduced. The above two reasons appear to be mainly responsible for their high supersaturation. The effect of stirring, which helps the entities to come together more frequently, supports this view. When stable nuclei are once formed, however, crystallisation starts because the strong surface forces outweigh the effects of the outer sheath and the process continues till the equilibrium is established.

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CHEMICAL LABORATORY,
THE UNIVERSITY,
LUCKNOW.

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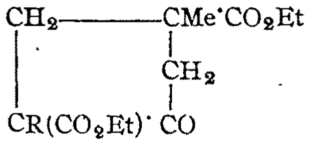
# ACTION OF SODIUM ON ETHYL β-METHYLBUTANE-αβδ-TRICARBOXYLATE. PART II. STRUCTURE OF THE ETHYLATED CONDENSATION PRODUCT

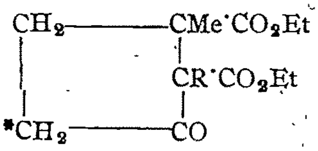
By Ram Narayan Chakravarti

The product of the action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate on ethylation furnishes ethyl 3-methyl-5-ethyl*cyclo*pentan-1-one-3 : 5-dicarboxylate, since on hydrolysis it affords β-methyl-*n*-hexane-αβδ -tricarboxylic acid, m. p. 172-73°, which Baker was unable to obtain in a state of purity. The structure of the latter is rigidly proved by rational synthesis. An independent synthesis of the isomeric γ-methyl-*n*-hexane-αγδ tricarboxylic acid, m. p. 169°, is also described.

In part I (Chakravarti, *J. Indian Chem. Soc.*, 1943, **20**, 173) it has been shown that ethyl β-methylbutane-αβδ-tricarboxylate on sodium condensation followed by methylation of the resulting sodio-salt gives ethyl 3 : 5-dimethyl*cyclo*pentan-1-one-3 : 5- dicarboxylate (I, R=Me) as the sole product, apparently no trace of the isomeric ethyl 2 : 3-dimethyl*cyclo*pentan-1-one-2 : 3-dicarboxylate (II, R=Me) could be detected.



(I)



(II)

Baker (*J. Chem. Soc.*, 1931, 1548) was, however, unable to ethylate the above Dieckmann condensation product with sodium ethoxide and ethyl iodide in the usual way although this difficulty was overcome by the use of sodamide in dry ether and a large excess of ethyl iodide. The ethylated product was formulated as (II, R=Et) since on hydrolysis with alcoholic potash it gave γ-methyl-*n*-hexane-αγδ -tricarboxylic acid (III, $R_1$=H , $R_2$=Et), m. p. 155°, the structure of which was not rigidly proved. In view of this discrepency it seemed desirable to re-examine Baker's work in the light of the facts already ascertained.

$$CO_2H{\cdot}CHR_1{\cdot}CH_2{\cdot}CMe(CO_2H){\cdot}CHR_2{\cdot}CO_2H$$

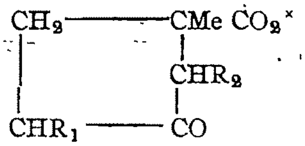
(III)

In the first instance by carrying out the ethylation of the Dieckmann product *in situ* with ethyl iodide in the usual way, the difficulties which rendered the experiments of Baker so laborious have been entirely obviated. The ethylated ester gives no colouration with ferric chloride and on hydrolysis with alcoholic potash yields a tricarboxylic acid, m p. 155°, along with a little gummy substance from which no crystalline product could be isolated. On repeated crystallisation from concentrated hydrochloric acid the tricarboxylic acid melts sharply at 172-73°. On hydrolysis with hydrochloric acid, on the other hand, the ethyl ester gives an acidic product consisting for the most part of a liquid keto-acid which apparently gives a homogeneous semicarbazone, m. p. 191°. Since Baker (*loc. cit.*) represented the tricarboxylic acid as γ-methyl-*n*-

hexane-αγδ-tricarboxylic acid it seemed desirable to prepare a specimen of this acid, for direct comparison, by an unambiguous method.

$CO_2Et{\cdot}CHR_1{\cdot}CH_2{\cdot}CMe(CN){\cdot}CR_2(CN){\cdot}CO_2Et$

(IV)



(V)

Ethyl αβ-dicyano-β-methylbutane-αδ-dicarboxylate (IV, $R_1=R_2=H$; Banerjee, *J. Indian Chem. Soc.*, 1940, **18**, 425) is ethylated with ethyl iodide and sodium ethoxide to give ethyl γδ-dicyano-γ-methyl-*n*-hexane-αδ-dicarboxylate (IV, $R_1=H$; $R_2=Et$). The latter on hydrolysis with concentrated hydrochloric acid furnishes γ-methyl-*n*-hexane-αγδ-tricarboxylic acid (III, $R_1=H$; $R_2=Et$), m. p. 169°. The latter proves to be quite different from the tricarboxylic acid, m. p. 173°, derived from the ethylated ester (see above) since they show a mutual depression of their melting points when mixed. The triethyl ester (as III, $R_1=H$; $R_2=Et$) is allowed to react with sodium and the resulting ethyl 2-ethyl-3-methly*cyclo*pentan-1-one-3 : 5-dicarboxylate (V, $R_1=CO_2Et$; $R_2=X=Et$) is hydrolysed to give 2-ethyl-3-methyl*cyclo*pentan-1-one-3-carboxylic acid (V, $R_1=X=H$; $R_2=Et$) which is directly converted into the semicarbazone m. p. 213-14°. Evidently, therefore, the keto-acid (V, $R_1=X=H$; $R_2=Et$) must be different from the isomeric acid (V, $R_1=Et$; $R_2=X=H$) isolated from the ethylated ester.

It follows, therefore, that the crystalline tricarboxylic acid, m. p. 172-73°, must be correctly represented as β-methyl-*n*-hexane-αβδ-tricarboxylic acid (III, $R_1=Et$; $R_2=H$). The latter has accordingly been synthesised by the process outlined in the following scheme. Ethyl α-ethyl-laevulate (VI) (Thorne, *J. Chem. Soc.*, 1881, **39**, 337; Young, *Annalen*, 1883, **216**, 340) is condensed with ethyl cyanoacetate in presence of acetamide and acetic acid (*cf.* Cope, *J. Amer. Chem. Soc*, 1937, **59**, 2329) to give ethyl α-cyano-β-methyl-$\Delta^{\alpha}$-hexene-αδ-dicarboxylate (VII). The latter on treatment with hydrogen cyanide furnishes ethyl αβ-dicyano-β-methyl-*n*-hexane-αδ-dicarboxylate (IV, $R_1=Et$; $R_2=H$) (*cf.* Hope and Sheldon, *J. Chem. Soc.*, 1922, **121**, 2223; Lapworth and McRea, *ibid.*, p. 2752; also Bardhan and Ganguly, *ibid.*, 1936, 1852), which is smoothly hydrolysed to β-methyl-*n*-hexane-αβδ-tricarboxylic acid (III, $R_1=Et$; $R_2=H$), m. p. 173°, alone or in admixture with the tricarboxylic acid obtained from the ethylated ester.

$CO_2Et{\cdot}CHEt{\cdot}CH_2{\cdot}CO{\cdot}Me$ (VI)

$CO_2Et{\cdot}CHEt{\cdot}CH_2{\cdot}CMe{:}C(CN){\cdot}CO_2Et$ (VII)

The corresponding triethyl ester (III, $R_1=Et$; $R_2=H$) on treatment with sodium gives ethyl 3-methyl-5-ethyl*cyclo*pentan-1-one-2:3-dicarboxylate (V, $R_1=X=Et$; $R_2=CO_2Et$). This on hydrolysis with dilute acid affords 3-methyl-5-ethyl*cyclo*pentan-1-one-3-carboxylic acid (V, $R_1=Et$; $R_2=X=H$) as a liquid which is characterised by the preparation of a semicarbazone, m. p. 191°, identical in all essential respects with the semicarbazone of the keto-acid obtained from the ethylated ester.

Clearly, therefore, the tricarboxylic acid, m. p. 173°, derived from the ethylated ester must be represented as β-methyl-*n*-hexane-αβδ-tricarboxylic acid (III, $R_1=Et$; $R_2=H$) Consequently the ethylated ester should be formulated as (I, $R=Et$). Since Baker's ethylated ester exhibits no colouration with ferric chloride, there can be no question that Dieckmann ester

(II, R=H) behaves in an abnormal manner in presence of sodamide and ethylates at the carbon atom marked (*) leading to the formation of the keto-ester (V, $R_1$=Et ; $R_2$=$CO_2Et$ ; X=Et) which can of course afford β-methyl-*n*-hexane-αβδ-tricarboxylic acid (III, $R_2$=H; $R_1$=Et) on hydrolysis.

## EXPERIMENTAL

*Sodium Condensation of Ethyl β-Methylbutane-αβδ-tricarboxylate and Ethylation of the Sodio-salt. Formation of Ethyl* 3-*Methyl*-5-*ethyl*cyclo*pentan*-1-*one*-3:5-*dicarboxylate* (I, R=Et) —Ethyl β-methylbutane-αβδ-tricarboxylate required for the purpose was prepared by a modification of Ruzicka's method (Chakravarti, *loc. cit.*) The triethyl ester (10·8 g.) was heated on the water-bath for 1 hour with finely divided sodium (1·03 g.) suspended in dry benzene (25 c.c.). The clear solution obtained was cooled in ice, treated with ethyl iodide (5 c.c.) and kept overnight. Next day, another 5 c.c. of ethyl iodide were added to it and it was refluxed for 24 hours The product was treated with water, the benzene layer was separated, washed and the benzene distilled off under reduced pressure. The product distilled at 142°/6mm., yield 8·8g. It gave no colouration with alcoholic ferric chloride. (Found : C, 62·0 ; H, 8·0 $C_{14}H_{22}O_5$ requires C, 62·2 ; H, 8·1 per cent).

*Acid Hydrolysis of the Ethylated Product. Formation of β-Methyl*-n-*hexane-αβδ-tricarboxylic Acid* (III, $R_1$=Et ; $R_2$=H) —The above product (4 g.) was heated on a water-bath for 3 hours with potassium hydroxide (4 g.) in 25% aqueous alcoholic solution. The alcohol was then evaporated off with the addition of water. The alkaline solution was acidified, saturated with salt and extracted with ether, and the solid residue obtained on evaporation of the ether was crystallised several times from concentrated hydrochloric acid, The acid melted at 172-73° (mixed m. p. with an authentic specimen of β-methyl-*n*-hexane-αβδ-tricarboxylic acid). A mixture of this acid with pure γ-methyl-*n*-hexane-αγδ-tricarboxylic acid melted gradually from 148-58°. (Found : C, 51·4 ; H, 6·9. $C_{10}H_{16}O_6$ requires C, 51·7 ; H, 6·9 per cent).

*Ketonic Hydrolysis of the Ethylated Product : Formation of* 3-*Methyl*-5-*ethyl*cyclo*pentan*-1-*one*-3-*carboxylic Acid* (V, $R_1$=Et ; $R_2$=X=H).—The ethylated product (4 g.) was heated on a sand-bath for 16 hours with 8% aqueous hydrochloric acid (40 c.c.). It was neutralised with sodium carbonate and extracted with ether to remove any neutral matter. The aqueous solution was then acidified, saturated with salt and extracted with ether. The liquid acid obtained on evaporation of the ether was converted into the *semicarbazone*. It crystallised in needle-shaped crystals and melted with decomposition at 191° after two crystallisations from methyl alcohol, (mixed melting point with an authentic sample of the semicarbazone of 3-methyl-5-ethyl*cyclo*pentan-1-one-3-carboxylic acid). (Found. C, 52·5 ; H, 7·4. $C_{10}H_{17}O_3N_3$ requires C, 52·8, H, 7·5 per cent)

*Synthesis of γ-Methyl*-n-*hexane-αγδ-tricarboxylic Acid* (III, $R_1$=H ; $R_2$=Et) *and* 3-*Methyl*-2-*ethyl*cyclo*pentan*-1-*one*-3-*carboxylic Acid* (V, $R_1$=X=H ; $R_2$=Et).—Ethyl αβ-dicyano-β-methylbutane-αδ-dicarboxylate required for the purpose was prepared according to Banerjee (*loc cit.*).

*Ethyl γδ-Dicyano-γ-methyl*-n-*hexane-αδ-dicarboxylate* (IV, $R_1$=H ; $R_2$=Et).—This was prepared by adding ethyl αβ-dicyano-β-methylbutane-αδ-dicarboxylate (19·95 g.) to an ice-cold solution of sodium (1.72 g.) in absolute alcohol (28 c.c.). Ethyl iodide (10 c.c.) was then added to it and it was kept overnight. The reaction was completed by refluxing on the water-bath for 24 hours. The product was diluted with water and the oily liquid separating was taken up in ether and distilled. The product was obtained as a colourless mobile liquid boiling at 175°/5 mm., yield 17·5 g. (Found : C, 60·9 ; H, 7·4. $C_{15}H_{22}O_4N_2$ requires C, 61·2 ; H, 7·4 per cent).

*γ-Methyl*-n-*hexane-αγδ-tricarboxylic acid* (III, $R_1 = H$ ; $R_2 = Et$).—The above product (16 g.) was hydrolysed by heating on a sand-bath for 25 hours with 5 volumes of concentrated hydrochloric acid. The clear solution obtained was evaporated completely to dryness and extracted with ether. The residue obtained on evaporation of the ether was esterified by the alcohol-vapour method in the usual way. The product distilled at 150°/5mm , yield 8g. (Found C, 60·4 ; H, 8·7. $C_{16}H_{28}O_6$ requires C, 60 7 ; H, 8·8 per cent).

The *pure* acid was obtained by hydrolysing the triethyl ester with excess of concentrated hydrochloric acid till a clear solution was obtained. It was then evaporated to dryness on the water-bath and the solid acid obtained was crystallised several times from concentrated hydrochloric acid. It melts at 169°. (Found : C, 51·4 ; H, 6 8. $C_{10}H_{16}O_6$ requires C, 51·7 ; H, 6·9 per cent).

*Ethyl 3-methyl-2-ethyl*cyclo*pentan-1-one-3:5-dicarboxylate* (V, $R_1 = CO_2Et$ ; $R_2 = X = Et$).—The above triethyl ester (3·6 g.) was heated on the water-bath with molecular sodium (0·37 g ) suspended in dry benzene (12 c.c.). The reaction started on heating and was complete in 1 hour. It was then treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed well with water and the benzene evaporated. The residual oil on distillation gave ethyl 3-methyl-2-ethyl*cyclo*pentan-1-one-3:5-dicarboxylate (2·45 g.), b. p. 150°/8mm. It gave a deep violet colouration with alcoholic ferric chloride. (Found : C, 61·8 ; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2 ; H, 8·1 per cent).

*3-Methyl-2-ethyl*cyclo*pentan-1-one-3-carboxylic Acid* (V, $R_1 = X = H$ ; $R_2 = Et$).—The keto-dicarboxylic ester (2·3 g.) was hydrolysed by heating on a sand-bath for 12 hours with 6 % aqueous hydrochloric acid (30 c.c.). It was then neutralised with sodium carbonate and extracted with ether to remove any neutral matter. The aqueous solution was then acidified, saturated with salt and extracted with ether. The crude keto-acid was obtained as a liquid on evaporation of the ether. The *semicarbazone* was readily obtained by treating the product in a little spirit with a concentrated aqueous solution of semicarbazide acetate. It crystallises from dilute methyl alcohol as a microcrystalline powder, m. p. 213-14° (decomp.) (Found : C, 52·7 , H, 7·7. $C_{10}H_{17}O_3N_3$ requires C, 52·8 ; H, 7·5 per cent).

Pure *3-methyl-2-ethyl*cyclo*pentan-1-one-3-carboxylic acid* (V, $R_1 = X = H$ ; $R_2 = Et$) was obtained as a crystalline solid on hydrolysing the semicarbazone with dilute hydrochloric acid (1:2). The mixture was gently heated on the water-bath till a clear solution was obtained. The solution was then saturated with salt and extracted with ether. The solvent was then evaporated completely and the solid residue after drying on a porous plate was purified by crystallisation from petroleum ether containing a little benzene, m.p. 91°. (Found C, 63·4 ; H, 8·2. $C_9H_{14}O_3$ requires C, 63·5 ; H, 8·2 per cent)

*Synthesis of β-Methyl*-n-*hexane-αβδ-tricarboxylic Acid* (III, $R_1 = Et$; $R_2 = H$) *and 3-Methyl-5-ethyl* cyclo *pentan-1-one-3-carboxylic Acid* (V, $R_1 = Et$ ; $R_2 = X = H$).—Ethyl α-ethyllaevulate, was prepared after Thorne (*loc. cit.*), with some modifications by condensing the sodio-salt of ethyl acetoacetate with ethyl α-bromobutyrate. Hydrolysis of the product was effected with dilute hydrochloric acid (*cf.* also Young, *loc cit* ) and α-ethyl laevulic acid, thus obtained, was esterified in presence of hydrogen chloride.

Ethyl acetoacetate (35·7 g.) was added drop by drop to an ice-cold suspension of finely divided sodium (6·32 g.) in benzene (70 c.c.) and then kept overnight. Next day, ethyl α-bromobutyrate (53·6 g.) was added to it and it was refluxed on the water-bath for 20 hours. It was then treated with water, the benzene layer was separated, washed and the benzene evaporated. The residual oil was then distilled in *vacuo*, b.p. 122°/6mm , yield 38·5 g.

Ethyl α-acetyl-β-ethylsuccinate, thus obtained, was heated on a sand-bath for 20 hours with 5 volumes of dilute hydrochloric acid (1·2). It was then evaporated completely on the water-bath. The dry liquid residue (17 g.) was heated on the water-bath for 10 hours with absolute alcohol (80 c.c.) and 8 c.c. of alcoholic hydrogen chloride (saturated at 0°). The alcohol was then distilled off and the product was taken up in ether, washed with dilute sodium carbonate solution and water and the ether evaporated. The residual liquid gave ethyl α-ethyllaevulate (16 g.), b. p. 88°/6mm.

*Ethyl α-Cyano-β-methyl-*$\Delta^{\alpha}$*-hexene-αδ-dicarboxylate* (VII).—Ethyl α-ethyllaevulate (15·9 g.) was mixed with ethyl cyanoacetate (10·5 g.), acetamide (2 g.) and glacial acetic acid (35 c.c.). The acetic acid was distilled off slowly during 6 hours, so that the temperature of the vapour was between 105° and 115°. The product was taken up in ether, washed with water and the ether evaporated. The liquid remaining was then distilled in *vacuo*, when with the exception of some unchanged product below 100°/5mm., it boiled at 150°/5mm., yield 16 g. (Found : C, 62·7 ; H, 7·8. $C_{14}H_{21}O_4N$ requires C, 62·9 ; H, 7·8 per cent).

*Ethyl αβ-dicyano-β-methylhexane-αδ-dicarboxylate* (IV, $R_1$=Et ; $R_2$=H) was prepared by treating the above unsaturated cyano-ester (15·7 g.) in spirit (75 c.c.) with a solution of potassium cyanide (7·7 g.) in water (42 c.c.). It was cooled in ice-water and 20% hydrochloric acid (16 c.c.) was added drop by drop. It was then kept for 45 minutes allowing it to attain the room temperature. It was finally diluted with water, acidified with hydrochloric acid and the oil separating was taken up in ether and washed. On evaporation of the solvent a light yellow oily liquid was obtained which boiled at 170°/4 mm., yield 14·3 g. (Found : C, 61·4 ; H, 7·2. $C_{16}H_{22}O_4N_2$ requires C, 61·2 ; H, 7·4 per cent).

*β-Methyl-n-hexane-αβδ-tricarboxylic Acid* (III, $R_1$=Et ; $R_2$=H).—The above product (13·9 g.) was heated on a sand-bath for 12 hours with concentrated hydrochloric acid (75 c.c ). The clear solution, thus obtained, was evaporated to dryness and the solid residue extracted with ether. The solid product obtained on evaporation of the ether after several crystallisations from concentrated hydrochloric acid melted at 173°. The *pure* acid is readily soluble in water and hot concentrated hydrochloric acid, but sparingly soluble in ether and insoluble in light petrol. (Found : C, 51·5 ; H, 6·9. $C_{10}H_{16}O_6$ requires C, 51·7 ; H, 6·9 per cent).

The *triethyl ester* was prepared by heating the acid (10 g.) at 110° for 6 hours with absolute alcohol (30 c.c.) and concentrated sulphuric acid (3 c.c.) in a current of hot alcohol vapour. The product was then worked up and distilled in the usual way, b. p. 140°/5mm., yield 10·5 g. (Found : C, 60·6 ; H, 8·7. $C_{16}H_{28}O_6$ requires C, 60·7 ; H, 8·8 per cent).

*Ethyl 3-methyl-5-ethyl*cyclo*pentan-1-one-2:3-dicarboxylate* (V, $R_1$=X=Et; $R_2$=$CO_2$ Et) was prepared by heating the triethyl ester (10·3 g.) on the water-bath with a fine suspension of sodium (0·92 g.) in benzene (25 c.c.). The reaction started on heating and was complete in ½ hour. The product was treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed well with water and the benzene evaporated. The residual oil distilled at 130°/5mm., yield 6·5 g It gives a violet colouration with alcoholic ferric chloride. (Found : C, 62·1 ; H, 8·1 $C_{14}H_{22}O_5$ requires C, 62·2 ; H, 8·1 per cent).

3-*Methyl-5-ethyl*cyclo*pentan-1-one-3-carboxylic Acid* (V, $R_1$=Et; $R_2$=X=H).—The above product (6·2 g.) was heated on a sand-bath for 10 hours with 6% hydrochloric acid (70 c.c.). The product was neutralised with sodium carbonate and extracted with ether to remove any neutral matter. It was then acidified, saturated with salt and extracted with ether. The acid was obtained as a liquid on evaporation of the ether The *semicarbazone* crystallises from methyl alcohol as colourless needles, m.p. 191°. (Found: C, 52·5; H, 7·4. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·5 per cent)

The *ethyl ester* was prepared by heating the keto-acid with absolute alcohol in presence of hydrogen chloride. It is a colourless liquid, b. p. 110°/8 mm. The *semicarbazone* of the ethyl ester crystallises from dilute alcohol in colourless crystals, m.p., 142-43°. (Found: C, 56·2; H, 8·0. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·2 per cent).

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# A PRELIMINARY STUDY OF THE AGEING OF ALUMINA AND SILICA GELS AND OF THE PRECIPITATES OBTAINED FROM MUTUAL COAGULATION OF ALUMINA AND SILICIC ACID SOLS

By S. P. Raychaudhuri and Abul Hussain Miah

The buffer curves of freshly prepared gels of silica, alumina and of aluminosilicates of varying $SiO_2/Al_2O_3$ ratios have been compared with those of aged (for one year) ones and with those of the naturally occurring clay minerals like bauxite, halloysite, kaolin, limonite and montmorrillonite Freshly prepared substances are found to possess much less buffer capacity than the aged ones With freshly prepared materials the buffer capacity passes through a maximum value with increasing $SiO_2/Al_2O_3$ ratios, whilst with aged ones the buffer capacity continuously increases as the $SiO_2/Al_2O_3$ ratios of the precipitates increase, attaining a maximum value with pure silica gel.

Noll (*Ber. deut. Keram. Gessel.*, 1938, **19**, 176, and earlier publications) has synthesised a number of clay-forming minerals by heating amorphous silica and alumina with aqueous or sodium hydroxide solution to 300°-500° in a hydrothermal bulb. In a very recent paper Raychaudhuri and Ghani (*J. Indian Chem. Soc.*, 1942, **19**, 311) have shown that freshly precipitated alumino-silicates resemble clay minerals like beidellite, montmorillonite, halloysite, etc., in all respects, except in base exchange properties and have suggested that ageing of the precipitates may be the cause of any difference in properties between clay minerals and the alumino-silicate precipitates.

It appears, however, that no systematic investigation has so far been carried out on the physicochemical properties of the naturally occurring alumino-silicates of different groups in relation to those of the freshly prepared and aged alumino-silicates of widely varying $SiO_2/Al_2O_3$ ratios. It was accordingly felt desirable to study, as a preliminary step, the nature of the buffer curves of the precipitates obtained by mixing alumina and silica sols and also of the gels of alumina and silica, along with those of the naturally occurring minerals, like bauxite, kaolin, montmorillonite, halloysite and limonite.

## EXPERIMENTAL

Electrodialysed precipitates of alumino-silicates and of silica and alumina, which were prepared and used by Raychaudhuri and Ghani (*loc. cit.*), have been used in the present investigation. The materials were kept in stoppered glass bottles for nearly one year. The buffer curves were determined by following the procedure adopted by Schofield (*J. Agric. Sci.*, 1933, **23**, 252).

The uptake of base in milli-equivalents per 100 g. of freshly prepared materials (oven-dry basis) are shown in Table IA (Fig. 1). The corresponding data with the same materials after they have been aged for one year are shown in Table IB (Fig. 2).

TABLE I

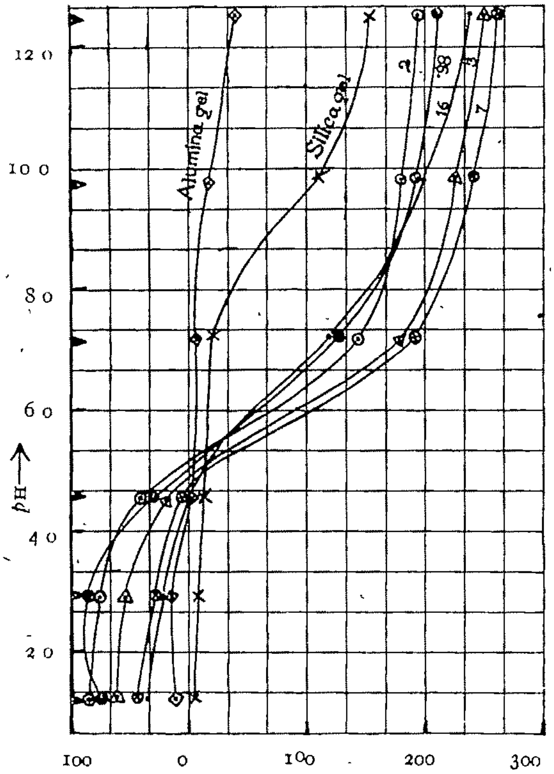
| Comp ratio ($SiO_2/Al_2O_3$) | *A. M. equiv. of base taken up per 100 g of freshly prepared precipitates (oven-dry basis) at | | | | | | B. M equiv of base taken up per 100 g of the precipitates after ageing for 1 year (oven-dry basis) at | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $p_H$1·3. | $p_H$2·9 | $p_H$4·6. | $p_H$7·1 | $p_H$9 8. | $p_H$12·5 | $p_H$1 3 | $p_H$2·9. | $p_H$4 6. | $p_H$7·1. | $p_H$9 8 | $p_H$12 5 |
| 0·98 | −73 | −87 | −30 | +125 | +188 | +208 | − 88 | −83 | −35 | + 98 | +235 | + 560 |
| 2·00 | −88 | −78 | −39 | +140 | +179 | +190 | − 74 | −69 | −51 | +105 | +253 | + 681 |
| 3 00 | −60 | −55 | −24 | +180 | +226 | +248 | −120 | −83 | −15 | +130 | +318 | + 714 |
| 7 00 | −43 | −30 | −10 | +193 | +238 | +263 | − 86 | −58 | ± 0 | +201 | +415 | + 957 |
| 16·00 | −35 | −27 | ± 0 | +120 | +194 | +238 | − 93 | −27 | ± 0 | +140 | +431 | +1031 |
| $Al_2O_3$ gel | −11 | −17 | + 1·0 | +2·0 | + 17 | + 37 | − 16 | −14 | −12 | + 39 | + 94 | + 144 |
| Silicic acid gel | + 2·0 | + 2 0 | + 7·0 | +13 | +107 | +149 | − 62 | −43 | −30 | + 99 | +620 | +1097 |

* The data have been quoted to appromimate whole numbers from the paper of Raychaudhuri and Ghani, *loc. cit.*

## DISCUSSION

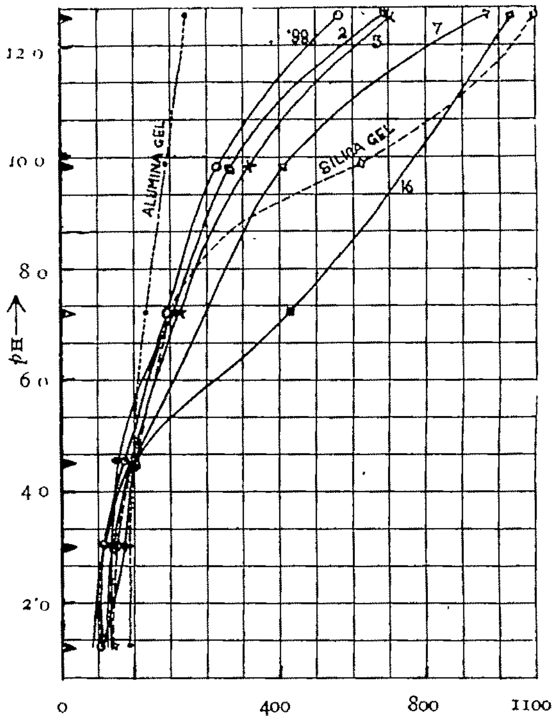
Figs. 1 and 2 show that the freshly prepared gels possess much less buffer capacity than the aged ones. Fig. 1 further shows that there is a maximum value in the buffer capacity at a certain composition ratio ($SiO_2/Al_2O_3 = 3{\cdot}0$) of the precipitate which is in agreement with the findings of Mattson (*Soil Sci.*, 1928, **25**, 289) and of Wiegner (*J. Soc. Chem. Ind*, 1931, **50**, 65T, 103T). The curves in Fig. 2 show, however, that with aged gels the buffer capacity is least with pure alumina gels and increases as the ratio of silica to alumina in the precipitate increases. Ageing therefore brings about certain fundamental changes in the structure of the gels, such that the greater the proportion of silicic acid anions in the aged precipitates, the more open is the soil structure, pure silicic acid gels having the maximum open structure.

FIG. 1



M. equiv. of base taken up per 100g ppt.

FIG. 2



M. equiv of base taken up by 100 g ppt.

[Nos. against the curve refer to ratio of $SiO_2/Al_2O_3$]

The figure shown in the paper of Raychaudhuri and Basuraychaudhuri (*Indian J. Agric. Sci.*, 1942, **12**, 146), shows the nature of buffer curves of clay-forming minerals. The curves there, are similar to those in Fig. 2, which suggests that ageing of the gels favours the formation of these minerals. It would appear from the figure shown by Raychaudhuri and Basuraychaudhuri (*loc. cit.*) that contrary to our expectations, the buffer capacity of montmorillonite is less than that of kaolin. It is likely therefore that montmorillonite has to be powdered to a much finer state of subdivision than kaolin (in the present experiments both kaolin and montmorillonite were powdered to 100 mesh), if comparable results of base exchange capacity are to be obtained.

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# ON THE RELATION BETWEEN SURFACE TENSION AND VAPOUR PRESSURE OF LIQUIDS AND LIQUID MIXTURES

By R. C. Tripathi

An equation of the type $\log p = A + \frac{B}{C-\gamma}$ (where $p$ is the vapour pressure, $\gamma$ is the surface tension of liquids and $A$, $B$ & $C$ are constants) is proposed and is shown to represent the variation of surface tension of unassociated, associated, organic and inorganic liquids with vapour pressure The same equation represents the variation of surface tension of binary liquid mixtures of constant composition with vapour pressure

No relation between the vapour pressure and surface tension of liquids seems to have been worked out. From the Clausius-Clapeyron equation connecting $Q$ (latent heat of evaporation), $p$ (vapour pressure), and $T$ (absolute temperature), it follows that

$$\log p = \frac{-Q}{RT} + A = A + \frac{B'}{T}.$$

Since surface tension varies linearly with temperature, at least for short ranges ($\gamma = C - mT$), an equation may be obtained by substituting $(C-\gamma)/m$ for $T$ in the above equation. The equation,

$$\log p = A + \frac{B}{C-\gamma}$$

where $A$, $B$ and $C$ are constants is obtained.

Table I gives in detail the results for ethyl ether (an unassociated liquid) and ethyl alcohol (an associated liquid). Other results are summarised in Table II where the constants $A$, $B$ and $C$ * are given along with the maximum percentage difference and $\gamma$ range in ($\gamma_{\text{max.}} - \gamma_{\text{min.}}$).

TABLE I

Ether.

$\gamma$-range = 30·36 $A$ = 8·21 $B$ = −209 1. $C$ = 54 1.

| Temp. | $p$. | $\gamma$ obs (dynes.) | $\gamma$ calc (dynes) | % Diff |
|---|---|---|---|---|
| −108° | 0·003 mm. | 33·25 | 33 20 | 0·1 |
| —94 75 | 0 12 | 31 58 | 31·30 | 0 9 |
| —93 4 | 0·15 | 31·23 | 30 90 | 1·0 |
| —85 2 | 0 33 | 30 04 | 30·00 | 0·1 |
| —80 4 | 0 58 | 29 47 | 29 40 | 0 4 |
| —63 | 2·90 | 27 32 | 27 13 | 0 6 |
| —45 05 | 13 | 24 91 | 24 60 | 1 3 |
| —18 85 | 63 | 21 46 | 21·13 | 1·3 |
| —20 | 412 | 16·49 | 16 50 | 0·1 |
| 40 | 648 | 14 05 | 14 20 | 1·0 |
| 50 | 1276 | 12 94 | 13 10 | 1 1 |
| 60 | 1728 | 11·80 | 12 00 | 1·6 |
| 70 | 2294 | 10 72 | 10 96 | 2 1 |
| 80 | 2991 | 9 67 | 9 76 | 0·9 |
| 90 | 3840 | 8·63 | 8·80 | 1 7 |
| 100 | 4859 | 7·63 | 7·80 | 2 0 |
| 150 | 13280 | 2·89 | 2·99 | 3·0 |

Ethyl alcohol

$\gamma$-range = 28·22. $A$ = 7 78. $B$ = −144 2. $C$ = 46·2.

| Temp | $p$. | $\gamma$ obs. (dynes) | $\gamma$ calc (dynes) | % Diff. |
|---|---|---|---|---|
| — 80° | 0·003 mm. | 32 21 | 31·90 | 0·9 |
| — 52·83 | 0 108 | 29·12 | 29·63 | 1·5 |
| — 43 | 0 25 | 28·11 | 28 70 | 2·1 |
| — 12 | 6 0 | 25·30 | 25 77 | 1 8 |
| — 80 | 812 | 16·61 | 16 60 | 0 0 |
| 100 | 1692 3 | 14·67 | 14 53 | 0 9 |
| 150 | 7326 | 9 52 | 9 40 | 1·3 |
| 200 | 22164 | 3 99 | 4 08 | 2 2 |

## TABLE II

### Liquid (organic)

| | Temp. range | *A* | —*B*. | *C*. | Max. diff. | γ-range |
|---|---|---|---|---|---|---|
| *cyclo*Hexane | 0−70 | 9·87 | 413 | 78·25 | 0·3% | 8·9 |
| Octane | 0−100 | 7·24 | 161·2 | 88·70 | 0·7 | 10·6 |
| Benzene | 0−250 | 9·43 | 406·5 | 82·50 | 3·2 | 29·3 |
| Toluene | −92−100 | 11·19 | 510·8 | 80·12 | 0·1 | 25·0 |
| *o*-Nitrotoluene | 80−172 | 6·16 | 138·6 | 60·20 | 0·3 | 10·6 |
| Chlorobenzene | 0−160 | 7·63 | 214·2 | 65·50 | 0·8 | 18·6 |
| Bromobenzene | −17−155 | 7·38 | 217 | 69·00 | 0·6 | 21·3 |
| Nitrobenzene | 53−175 | 5·26 | 83·7 | 55·50 | 0·1 | 14·1 |
| Aniline | 43−175 | 5·69 | 93·9 | 57·60 | 0·7 | 15·6 |
| *o*-Toluidine | 46−154 | 19·88 | 1948 | 136 | 0·4 | 12·8 |
| *m*-Toluidine | 50−150 | 6·17 | 112 | 53·80 | 0·1 | 9·9 |
| *p*-Toluidine | 46−126 | 13·38 | 706 | 17·54 | 0·2 | 6·5 |
| Ether | −108−150 | 8·20 | 209 | 54·10 | 2·7 | 30·4 |
| Carbon tetrachloride | 15−250 | 8·21 | 251·2 | 66·90 | 1·7 | 24·5 |
| Chloroform | −24−54 | 12·26 | 653 | 91·80 | 0·4 | 10·3 |
| Acetone | −91−30 | 7·32 | 181·4 | 58·55 | 0·8 | 15·8 |
| Methyl alcohol | −66−200 | 7·56 | 130·4 | 46·30 | 1·2 | 27·8 |
| Ethyl alcohol | −80−240 | 7·78 | 144·2 | 46·21 | 2·5 | 28·2 |
| Propyl alcohol | −23−100 | 9·65 | 205 | 47·00 | 0·1 | 9·6 |
| Butyl alcohol | 20−120 | 7·67 | 119·2 | 41·26 | 0·8 | 8·3 |
| *iso*Amyl alcohol | 0−130 | 7·99 | 135·8 | 41·40 | 1·6 | 9·9 |
| Ethyl formate | −20−210 | 6·78 | 101·0 | 43·95 | 1·8 | 23·6 |
| Ethyl acetate | 0−80 | 12·99 | 661·5 | 82·50 | 0·1 | 8·7 |
| Propyl acetate | −10−210 | 7·72 | 178·4 | 51·90 | 2·2 | 22·4 |
| Methyl *iso*butyrate | 0−210 | 6·62 | 106·3 | 44·90 | 1·2 | 21·8 |
| Methyl formate | 20−200 | 9·42 | 414·3 | 86·10 | 0·5 | 23·8 |
| Formic acid | 0−130 | 5·10 | 49·2 | 50·70 | 0·8 | 13·3 |
| Acetic acid | 0−110 | 20·32 | 1598 | 110·40 | 3·0 | 10·9 |
| Propionic acid | 10−140 | 8·01 | 188·6 | 51·59 | 0·7 | 12·7 |
| Butyric acid | 10−160 | 10·19 | 335·7 | 59·50 | 0·1 | 14·1 |
| Ethyl iodide | 0−60 | 6·27 | 104·1 | 52·80 | 0·7 | 6·7 |
| Capronic acid | 60−130 | 4·47 | 37·8 | 31·56 | 0·1 | 6·4 |
| Caprinic acid | 120−170 | 5·12 | 35·5 | 27·75 | 0·1 | 3·0 |
| Caprylic acid | 100−150 | 6·13 | 73·8 | 34·05 | 0·1 | 3·8 |

### Liquid (inorganic)

| | Temp. range | *A* | —*B*. | *C*. | Max. diff. | γ-range |
|---|---|---|---|---|---|---|
| Mercury | 20−360 | 5·29 | 322·5 | 511 | 0·1 | 95·2 |
| Zinc | 490−641 | 6·13 | 601 | 88·70 | 0·0 | 27·5 |
| Arsenic trichloride | 0−100 | 7·94 | 187·2 | 66·20 | 0·2 | 9·5 |
| Sodium fluoride | 1396−1557 | 5·01 | 191·4 | 216·1 | 0·0 | 14·8 |
| Caesium fluoride | 955−1118 | 1·15 | 13·8 | 67·15 | 0·1 | 8·0 |
| Phosphorus trichloride | −20−50 | 9·17 | 285 | 68·88 | 1·0 | 7·3 |
| Hydrochloric acid | −90−(−17) | 11·28 | 488 | 81·30 | 0·5 | 5·1 |
| Hydrobromic acid | −96−(−68) | 10·08 | 522 | 98·40 | 0·2 | 5·7 |
| Sulphuretted hydrogen | −62−84 | 4·36 | 27·15 | 46·50 | 0·1 | 4·7 |
| Chlorine | −75−50 | 6·80 | 127 | 59·60 | 0·2 | 20·15 |
| Helium | −271−(−268) | 59·85 | −331·8 | 5·95 | 2·0 | 0·3 |
| Neon | −249−(−243) | −0·95 | 1·15 | 3·525 | 1·4 | 1·6 |
| Oxygen | −205−(−182) | 7·27 | 104·6 | 36·95 | 0·7 | 5·5 |
| Carbon dioxide | −57−30 | −9·98 | 1996 | −168·7 | 0·1 | 18·1 |
| Sulphur dioxide | 0−50 | 3·73 | 132·8 | 64 | 0·1 | 9·8 |
| Nitrogen | −206−(−173) | 7·37 | 86·85 | 28·17 | 0·5 | 7·0 |
| Nitrous oxide | −88−20 | 27·13 | 0710 | 384 | 2·5 | 24·6 |
| Water | −0−80 | 5·51 | 101·4 | 96·4 | 0·3 | 13·2 |

It is evident from the tables that this equation is very satisfactory. It represents the variations of surface tension with vapour pressure in some cases from very near the freezing point to temperatures much above the boiling point with an error hardly exceeding 1% in most cases and never exceeding 3%. Moreover, the equation is applicable to organic, inorganic, simple and associated liquids.

Another remarkable feature of this equation is that it seems to apply not only to single liquids but also to liquid mixtures (comprising either simple liquids or associated liquids) of fixed composition in the same way as it does in the case of single liquids. The greatest difficulty in varifying this equation in the case of mixtures is that no data are available regarding the surface tension of the liquid mixtures at different temperatures. The values of surface tension of mixtures of any composition at any temperature can be calculated if they obey the mixture law with respect to parachor. A number of such mixtures which obey the mixture law with respect to parachor are known (Hammick and Andrew, *J. Chem. Soc.*, 1929, 754) and the present work on mixtures has been confined to these only. In Table III the percentage difference refers to the values of surface tension obtained by applying mixture law with respect to parachor and that calculated by this equation.

TABLE III

Temp. range=0° to 70°.

| Ethyl ether in benzene. | | | | | Carbon tetrachloride in benzene. | | | | | Acetic acid in benzene. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mol. fraction. | *A.* | *−B* | *C.* | Max diff. | Mole fraction | *A.* | *−B.* | *C.* | Max. diff. | Mol fraction. | *A.* | *−B.* | *C* | Max. diff. |
| 0·0 | 9·43 | 406·5 | 82·50 | 3 0% | 0·0 | 9·43 | 406·5 | 82·50 | 3·0% | 0 0 | 9 43 | 406·5 | 82·50 | 3·0% |
| 0·2356 | 11·68 | 644·5 | 93·55 | 0·1 | 0·1 | 11·19 | 596·5 | 92·80 | 1·2 | 0·1 | 6 62 | 133·9 | 55·90 | 0·1 |
| 0·4267 | 11·76 | 655·0 | 90·40 | 0·1 | 0·5 | −5·98 | 485·0 | −34·20 | 0·2 | 0·5 | 11·47 | 633·5 | 97·60 | 0·1 |
| 0·7469 | 8·50 | 231·0 | 58 10 | 0 3 | 0·9 | 13·50 | 898·5 | 104·60 | 0·1 | 0·9 | 9 43 | 386·0 | 81·30 | 0·1 |
| 1 0 | 8·20 | 209·0 | 54·10 | 2·0 | 1·0 | 8·21 | 251·2 | 69·60 | 1·7 | 1 0 | 20·32 | 1598·0 | 110·40 | 3 0 |

All the data for surface tension and vapour pressure have been taken from Landolt Bornstein Tabellen (1923 Edition and subsequent additional volumes).

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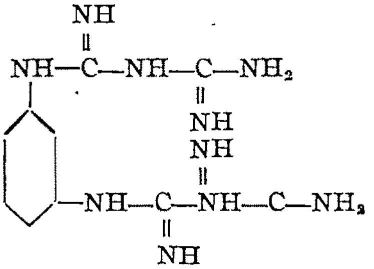
# COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART V. COPPER AND NICKEL *METAPHENYLENE*-DIBIGUANIDINE AND THEIR SALTS

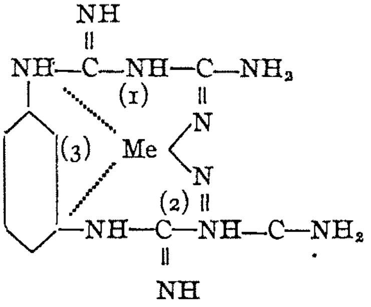
BY PRIYADARANJAN RÂY AND SUSHIL KUMAR SHIDDHANTA

*meta*Phenylenedibiguanide has been found to serve as a quadridentate molecule furnishing four points of attachment to a central metallic atom like copper and nickel. In the present paper a number of complex copper and nickel *meta*phenylenedibiguanide salts, besides the free bases, have been described, and the constitution of the complex discussed.

In course of a series of investigations on the complex compounds of metallic elements with biguanide and its substitution products, it is now found that *meta*phenylenedibiguanide (I) serves as a quadridentate molecule furnishing four points of attachment to a central metallic atom. Instances of quardridentate molecules in literature are rather few in number. Mention may be made of ethylenediamine-*bis*acetylacetone (Morgan and Mainsmith, *J. Chem. Soc.*, 1925, 2030), 2:2′:2″:2‴-tetrapyridyl (Morgan and Burstall, *ibid.*, 1937, 1649), $\beta\beta'\beta''$-triaminotriethylamine (Pope and Mann, *ibid.*, 1925, 834), ethylene *bis*thioglycollic ether (Reihlen, *Annalen*, 1926, **448**, 312), oxynaphthaldehyde ethylene, or *ortho*phenylenediamine and the corresponding salicylaldehyde derivatives (Pfeiffer ond Glaser, *J. prakt. Chem.*, 1939, **153**, 265). Porphyrin derivatives (chlorophyll and haemin) and phthalocyanine also belong to this class. *meta*Phenylenedibiguanide metal complex (II) presents certain interesting features from stereochemical point of view.



(I)



(II)

The central metal atom forms, as it were, the common link for the three fused six membered rings. If the 4-covalent metal atom forms, as supported by a large mass of physical and chemical evidences in the case of nickel and copper, a planar configuration, then this may either be in the same plane with the benzene ring or in a different one. In the former the fused ring (3) will be of irregular shape with a re-entrant angle, in the latter it will have a fold on one side. The tetrahedral configuration of copper in this case, resulting from the possible distortion of the ring due to partial dissemmetry of the molecule, is not, therefore, altogether excluded.

## EXPERIMENTAL

*Copper* meta*Phenylenedibiguanidine and its Hydroxide.*—*meta*Phenylenedibiguanide hydrochloride was prepared by heating in aqueous solution 1 mole of *meta*phenylenediamine hydrochloride and 2 moles of dicyandiamide. After the reaction the solution was made alkaline with ammonia and precipitated by ammoniacal copper sulphate solution. The crude complex sulphate was dissolved in the least quantity of dilute HCl and the complex base was precipitated from the solution by an excess of caustic potash. The precipitate was allowed to settle on the water-bath. This was washed and redissolved in the least amount of HCl and reprecipitated by KOH. The precipitate was then washed with hot water and dried over KOH. {Found : N, 36·92 ; Cu, 16·92, 16·96 ; $H_2O$, 9·58 (by loss at 110°). [Cu. Phen $(BigH^+)_2$] $(OH)_2$ requires N, 37·47; Cu, 17·02 ; $H_2O$, 9·64 per cent}.

The base was also prepared by the addition of KOH to a solution of the complex chloride. It forms dull brick-red powder, soluble partially in hot water, but readily in dilute mineral acids with decomposition. The substance is freely soluble in alcohol.

At about 110° it loses two molecules of water forming the anhydro-base, copper *meta*phynelenedibiguanidine, [Cu.Phen $(Big)_2$]. Phen$(BigH)_2$=one molecule of *meta*phenylenedibiguanide.

*The Complex Chloride.*—The crude complex base, obtained by precipitation with KOH from an acid (HCl) solution of the crude sulphate, was suspended in water and treated with an excess $NH_4Cl$ solution on the water-bath, till evolution of ammonia ceased. The resulting solution was left in the cold for several hours to crystallise. The product was purified by recrystallisation from hot water. The crystals were washed first with ice-cold water, then with alcohol and finally dried in air. {Found : N, 32·0 ; Cl, 16·35, 16·40 ; Cu, 14·66, 14·51. [Cu.Phen $(BigH^+)_2$] $Cl_2$, 1½ $H_2O$ requires N, 32·0 ; Cl, 16·20 ; Cu, 14·53 per cent}.

The substance forms dark blue-violet crystals, soluble in water and reacts neutral to litmus in the cold.

*Equivalent Conductivity at 32 6°*

| Dilution in litres ... | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| Λ, ... | 105·9 | 112·6 | 120·6 | 127·3 | 132·9 | 138·7 |

Λ∞ (mean) ... 137·35, from Walden's formula, $\Lambda\infty=\Lambda_v \; (1+n_1 \cdot n_2 \cdot 0{\cdot}692v^{-\frac{1}{2}})$.

Hence the mobility of the complex [Cu. Phen $(BigH^+)_2$] ion=137·35−86·0=51·35 at 32·6°. The substance hydrolyses slightly on dilution and reacts acid to litmus. This is also evident from the conductivity figures.

The *complex bromide* was prepared from a solution of the complex chloride and a cold concentrated solution of potassium bromide. The mixture was allowed to stand in the cold for several hours. The crystals were filtered, washed with ice-cold water and dried in air. {Found : Br, 30·09 ; Cu, 11·96. [Cu.Phen $(BigH^+)_2$]$Br_2$, $2H_2O$ requires Br, 29·82 ; Cu, 11·87 per cent.}. It forms violet crystals, difficultly soluble in water.

The *complex iodide* was obtained from the complex chloride and potassiam iodide as in the previous case. {Found : I, 42·60 ; Cu, 10·74, 10·78. [Cu.Phen $[BigH^+)_2$] $I_2$ requires I, 42·76 ; Cu, 10·71 per cent}. The substance forms dirty blue-violet crystals, moderately soluble in water.

The *complex nitrate* was prepared from a cold strong solution of the complex chloride and that of ammonium nitrate. The red-violet crystalline precipitate was washed and dried. {Found : Cu, 13·58, 13·61; $NO_3$, 26·13. [Cu.Phen $(BigH^+)_2$]$(NO_3)_2$, ½$H_2O$ requires Cu, 13·46 ; $NO_3$, 26·24 per cent}.

The *complex sulphate* was prepared from a hot solution of the complex chloride and that of sodium sulphate. The mixture was digested on the water-bath till the precipitate turned deep blue. This was washed with hot water, followed by alcohol and then dried in air. {Found :

Cu, 12·16, 12·18; $SO_4$, 18·14. $[Cu.Phen(BigH^+)_2]\ SO_4, \frac{1}{2}H_2O$ requires Cu, 12·10; $SO_4$, 18·25 per cent}. The substance forms deep blue crystals, sparingly soluble in water.

The *complex thiosulphate* was obtained as a dull violet crystalline precipitate from a cold solution of the complex chloride and that of sodium thiosulphate. It was washed and dried. {Found: Cu, 12·77, 12·72; $S_2O_3$, 22·36. $[Cu.Phen\ (BigH^+)_2]S_2O_3, 2\frac{1}{2}H_2O$ requires Cu, 12·80; $S_2O_3$, 22·56 per cent}.

The *complex thiocyanate* was prepared by adding an ice-cold solution of the complex chloride to that of an excess of ammonium thiocyanate. The mixture was cooled in ice. The resulting precipitate was washed with ice cold water and dried in air. It forms light greyish blue crystals, soluble in water and alcohol. It hydrolyses rather readily in a warm dilute aqueous solution. {Found: Cu, 13·51; S, 13·34. $[Cu.Phen\ (BigH^+)_2]\ (SCN)_2, H_2O$ requires Cu, 13·43; S, 13·52 per cent}.

*Nickel* meta-*Phenylenedibiguanidine and its Hydroxide.*—The complex base was prepared in the same way as the corresponding copper compound, using a solution of nickel sulphate in place of the copper salt. A little ammonium chloride was added before precipitating the base with caustic alkali to prevent precipitation of any nickel hydroxide. The substance forms buff-coloured crystals with a dull red tinge. It is insoluble in water, but slightly soluble in alcohol. (Found: N, 34·73; Ni, 14·35. $[Ni.\ Phen\ (BigH^+)_2]\ (OH)_2, 2H_2O$ requires N, 34·60; Ni, 14·50 per cent}.

It loses the two molecules of water of hydration (8·82%) at 85°-90° and the remaining two molecules of hydroxylic water at 110° forming the dehydrated base and the anhydro-base—nickel *m*-phenylenedibiguanidine—$[Ni.\ Phen\ (Big)_2]$, respectively.

*Nickel* m-*Phenylenedibiguanidinium Sulphate.*—The crude sulphate, as obtained during the previous preparation was dissolved in a little dilute $H_2SO_4$ and reprecipitated by the addition of ammonia, care being taken that the solution did not become alkaline. The precipitate was washed free from sulphate with cold water and then dried in air. {Found: Ni, 11·33; $SO_4$, 18·75. $[Ni.\ Phen\ (BigH^+)_2]\ SO_4, 5H_2O$ requires Ni, 11·27; $SO_4$, 18·44 per cent}.

The substance forms brown crystals, insoluble in water and alcohol.

Attempts to prepare the corresponding complex chloride led, however, to impure products, as the compound hydrolyses in aqueous solution and forms an oily or viscous mass. Neutralisation of the base with dilute HCl, followed by evaporation of the resulting solution to dryness, produced also no better results.

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# MAGNETIC STUDY OF COLOUR CHANGES IN COPPER CHLORIDE

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Changes in magnetic susceptibility of cupric chloride in aqueous and hydrochloric acid solutions have been studied with change of temperature (35°, 55° and 75°) and with change of Cl′ ions keeping the concentration nearly constant with respect to $CuCl_2$.

It is well known that cupric chloride changes colour from green to blue when a concentrated solution is diluted. There are many explanations for this colour change which we have given briefly in our first communication (*J. Indian Chem. Soc.*, 1942, **19**, 357). The more plausible of these explanations are due to

(*a*) Ostwald ("Grundlinien der anorganischen Chemie", Leipzig, 1900) who explains it on the basis of ionisation of molecules, suggesting that cupric ions are blue and $CuCl_2$ molecules are brown in colour. $CuCl_2$ (brown)$\longrightarrow$$Cu^{\cdot\cdot}$ (blue) + $2Cl'$ (colourless).

(*b*) Wiedermanns (*British Assoc. Rep.*. 1887, 346,) who attributes the colour change to solvation of the solute. $CuCl_2$ (brown) + $n$ $H_2O$$\longrightarrow$$CuCl_2$ + $nH_2O$ (blue).

(*c*) Donnan and Bassets (*J. Chem. Soc.*, 1902, **81**, 939) who attribute the colour change to the formation and dissociation of complex ions. $CuCl_4$ (brown)$\longrightarrow$$CuCl_2^{\cdot\cdot}$ (blue) + $2Cl'$.

In a previous communication (*loc. cit.*) we have shown that the magnetic susceptibility measurements are in favour of complex ion formation. Change of colour of the solution with change in temperature has also been noted and it has been found that the change is parallel to the of change in concentration. This effect was first studied by Coppet (*Ann. chim. phys.*, 1871, *iv*, **23**, 386) who showed that blue colour changed to bluish green and then to green at higher temperatures.

Here again the same views are put forward and are supported by various workers and are briefly given below.

The hydration theory of Ostwald is supported by Lewis (*Z. physikal. Chem.*, 1906, **56**, 223; 1905, **52**, 222), and Blitz (*ibid.*, 1902, **40**, 199), who showed that a rise of temperature should cause dissociation of the hydrated ion into a less hydrated or non-hydrated ion.

Hartley and others (*J. Chem. Soc.*, 1903, **82**, 401) from absorption band spectrum have shown that rise in temperature produces the same effect as an increased concentration. If the observed change were due to the formation of complexes between the solute and the solvent this would not be the case; as a change produced by rise in temperature on such complexes is just opposite to that produced by an increase in ion concentration.

Complex ion theory of Donnan and Basset is supported by Watkins and Denham (*J. Chem. Soc.*, 1919, **115**, 1269), who have shown that decrease in transport number with rise of temperature favours the complex ion theory. Jones and Anderson ("Absorption Spectra of Solutions", Washington, 1909) also supported the same explanation. Bhagwat (*J. Indian Chem. Soc.*, 1940, **17**, 53) also supports the complex ion theory.

If complex ion formation were the real cause of colour change, the addition of Cl′ ions to the solution would certainly favour the colour change. In this work we have studied the change of magnetic susceptibility with change of temperature, and with change of concentration of Cl′ ions in solution keeping the concentration with respect to $CuCl_2$ nearly constant.

To increase the concentration of Cl′ ions various concentrations of hydrochloric acid were employed and the different temperatures used were 35°, 55° and 75°.

## EXPERIMENTAL

Two solutions of $CuCl_2$ were prepared, one in water and the second in HCl and the concentration of $CuCl_2$ was kept the same in both *i.e.*, about 5%. Colour in HCl solution was green and in aqueous solutions it was blue. Different proportions of these solutions were mixed to give different strengths of HCl but the strength of $CuCl_2$ remained the same in all the solutions. In these solutions there was a colour change. This could only be due to changing strength of HCl in solution or concentration of HCl.

The susceptibility measurements were made on a modified form of Guoy's balance. To maintain various temperatures a silica tube, wound round with a heating coil, was used.

In the case of the solutions the susceptibilities have been calculated on the assumption that the magnetic susceptibility of the solution is equal to the sum of component susceptibilities.

$$\chi_s = \frac{\chi_{sol} - \chi_w(1 - C_s)}{C_s}$$

Where $\chi_s$, $\chi_w$ and $\chi_{sol}$ are magnetic susceptibilities of solute, solvent and solution, $C_s$ is the amount of solute in 1g. of the solution.

Magnetic susceptibility of the conductivity water which was used in the present work was $-0{\cdot}720 \times 10^{-6}$.

Cupric chloride (Merck's guaranteed reagent) was dehydrated according to the method of Sabatier (*Bull. Soc. Chim.*, 1889, *iii*, 1, 88). Its susceptibility was found out at 35°, 55° and 75° to be $8{\cdot}718 \times 10^{-6}$, $8{\cdot}204 \times 10^{-6}$ and $7{\cdot}725 \times 10^{-6}$ respectively.

Hydrochloric acid which was used in this work had susceptibility $-0{\cdot}661 \times 10^{-6}$ at all these temperatures

TABLE I

*Influence of* HCl *on the magnetic suceptibility of aq. soln. of* $CuCl_2$

| % Composition of the soln. by wt. | | | Normality of the acid in soln. | $\chi$ soln. × $10^6$ at 35°. | | Colour. | $\chi$ soln. × $10^6$ at 55°. | | Colour. | $\chi$ soln. × $10^6$ at 75°. | | Colour. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CuCl_2$. | HCl. | $H_2O$. | | Obs. | Calc. | | Obs. | Calc. | | Obs. | Calc. | |
| 4·20 | 30·68 | 65·12 | 8·400 | −0·229 | −0·305 | Green. | — | — | | — | — | |
| 4·30 | 25·13 | 70·57 | 6·885 | −0·225 | −0·299 | | −0·249 | −0·321 | Green | −0·301 | 0·342 | Green |
| 4·41 | 19·33 | 76·26 | 5·296 | −0·222 | −0·292 | | −0·248 | −0·321 | | −0·300 | 0·335 | |
| 4·54 | 13·25 | 82·21 | 3·630 | −0·218 | −0·284 | | −0·245 | −0·307 | | −0·298 | 0·329 | |
| 4·66 | 6·81 | 88·53 | 1·874 | −0·189 | −0·276 | Blue. | −0·244 | −0·300 | | −0·296 | 0·322 | |
| 4·73 | 3·45 | 91·82 | 0·245 | −0·188 | −0·271 | | −0·234 | −0·296 | Blue | −0·298 | 0·318 | |
| 4·80 | 0·00 | 95·20 | — | −0·187 | −0·266 | | −0·233 | −0·291 | | −0·294 | 0·314 | |

An examination of the table shows that until the concentration of HCl in the solution is 13·25% *i.e.*, corresponding to 4*N*-HCl there is a small regular increase in the difference between the observed and calculated susceptibility of solution. On further decrease in the concentration of HCl, the solution turns from green to blue and a new magnetic carrier ion is formed. The difference is great as compared to the previous readings which show the formation of a more paramagnetic ion. On plotting the graph we find that there is a break in the curve and the two parts of the curve correspond to two different colours exactly. There is a big gap in the susceptibility of the solutions in two parts showing sudden change in the composition of the solution. This sudden break can only be due to the formation of a new compound.

The theories of hydration and ionisation are ruled out on the basis of the work of previous workers and especially of Datta (*Phil. Mag.*, 1934, **18**, 585) who have shown that hydration cannot bring a change in magnetic moment and as long as ions in solution remain the same magnetic moment does not change also.

Table I also shows the effects of change of temperature. The solutions (5th and 6th), which are blue at 35°, gradually change to the green form and at 75° even the 7th soution is green.

This shows that rise in temperature brings about exactly the same change as is brought about either by increase in concentration of $CuCl_2$ or of $Cl'$ by the addition of HCl. This is in favour of the work of Coppet (*loc. cit.*).

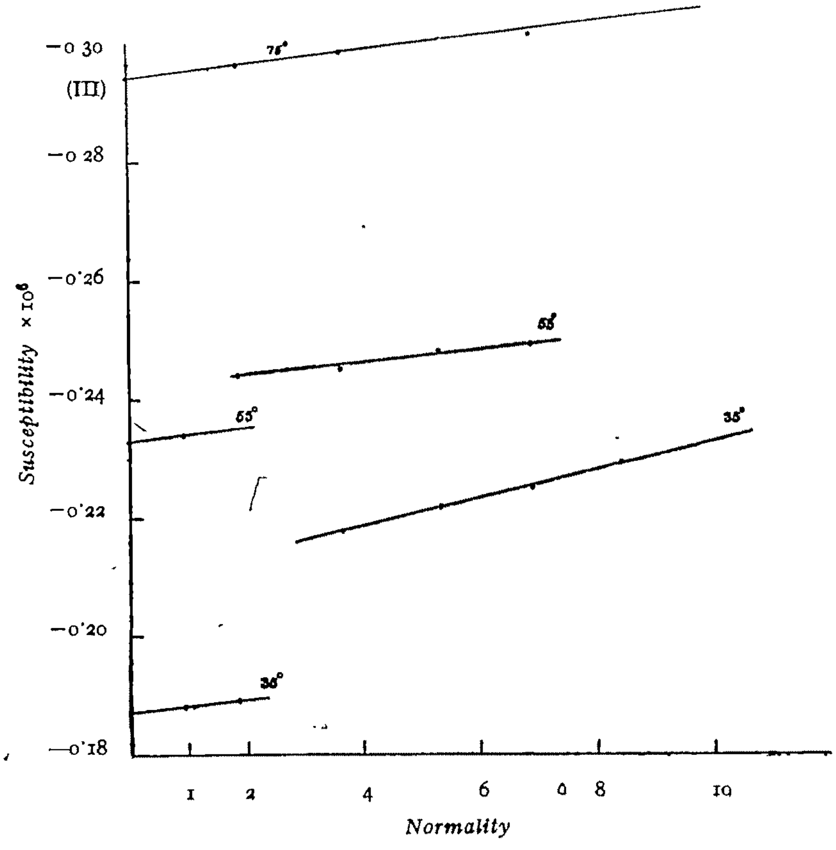

FIG. 1.

It has been shown by Jones and West also from the study of temperature coefficient that if the increase in concentration and rise in temperature produce the same effect it is due to the formation of complex ions of the type $CuCl_3$ and $CuCl_4$. Same results have been obtained by Bhagwat by studying the application of Beer's law.

We have not taken into account the small change in concentration of $CuCl_2$ in plotting these curves andthe same is the case in curve III ( 75°) which is absolutely a straight line. Had there been no colour change and no formation of new magnetic carriers, the other two curves would have been straight lines. The splitting up of first two curves into two different parts is simply due to the formation of new carrier ions which are more paramagnetic.

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# ON THE PHOTOCHEMICAL DECOMPOSITION OF PLATINUM COMPLEXES.
## PART I. PHOTOCHEMICAL DECOMPOSITION OF THE PLATINUM COMPLEXES WITH OXALIC ACID AND MALONIC ACID

By T. Banerjee, H. Chakravorty and S. Sarker

The photochemical decomposition of platinum complexes with oxalic and malonic acids has been studied. With malonic acid it was found that when the ratio, potassium malonate/chloroplatinic acid, was slightly greater than 3, the quantum efficiency jumped to a higher value and an induction period appeared, intensity of absorbed radiation remaining constant. 50% reduced Pt-complexes, reduced in *d*- or *l*-circularly polarised light, showed no optical activity.

The action of light upon the complex salts has been studied from the standpoint of Stark-Einstein law. The theory of optical activity by van't Hoff and the demonstration of Werner that some complex salts may exist in optically active forms have lent interest to the study of the photochemical properties of these compounds. Interesting possibilities centre round the action of polarised light, especially circularly polarised light, on complex compounds containing Pt *i.e.*, chelates containing tetravalent metallic ion. Investigations on the photochemical reaction kinetics of these complex compounds are likely to throw some light on the stability of such compounds and of the rings of dibasic organic acids and metallic ions in chelate compounds. The present investigation was thus undertaken with these objects in view.

## EXPERIMENTAL

The experimental arrangement and the method of measuring the intensity of radiation actually absorbed are the same as described by Banerjee (*J. Indian Chem. Soc.*, 1937, **14**, 61), and that for producing *d*- or *l*- circularly polarised light (366 $\mu\mu$) by Ghosh, Banerjee and Mukherjee (*ibid.*, p. 500). Kahlbaum's pure chloroplatinic acid of the formula $H_2PtCl_6$, $6H_2O$, was used. Schott and Gen ultraviolet filter No. 312 and Zeiss monochromats were used for isolating the regions 366 $\mu\mu$ and 436 $\mu\mu$ respectively. The amount of chloroplatinic acid present was determined iodometrically. There was no dark reaction in 10 hours.

It is evident from Table I that with the blue light the reactions follow the unimolecular law. But in the ultraviolet the unimolecular velocity constants obtained decrease slightly with time. Hence in the latter case the velocity constant and also the quantum efficiency ($\gamma$) have been calculated for one hour (after the termination of the induction period).

The velocity of reaction (Table II) is independent of the concentration of potassium bioxalate, even when the ratio reductant/oxidant changes from 10 to 3.

The apparent increase of velocity constant with increase in the concentration of chloroplatinic acid (Table III) is due to the corresponding increase in the amount of absorbed radiation ($P/Q_1$=constant).

The ratio $P/Q$ shows that the velocity of reaction varies directly as the intensity of absorbed radiation (Table IV).

*d*- and *l*-Circularly polarised lights were found to be practically equally efficient. In our experiments in the ultraviolet light, it has been observed that the unimolecular velocity constant decreases with time. So it was thought undesirable to attach any importance to the value of the unimolecular velocity constants obtained with *d*- or *l*-circularly polarised light when the

*Photochemical Decomposition of Complexes formed by Chloroplatinic Acid and Bioxalate of Potassium.*

TABLE I

*Determination of the order of reaction.*

Chloroplatinic acid = 0·01*M*. Potassium oxalate = 0·12*M*. Temp. = 26°. $Na_2S_2O_3$ soln. = 0·0125*M*. λ = the wave-length of incident light. $k_1$ = velocity constant.

| λ. | Time. | $Na_2S_2O_3$ soln. * | $k_1$. |
|---|---|---|---|
| 366 μμ | 0 min. | 1·7 c.c. | |
| | 60 | 1·6 | $1·8 \times 10^{-5}$ |
| | 120 | 1·51 | 1·6 |
| | 180 | 1 44 | 1 4 |
| | 240 | 1·38 | 1·2 |
| 436 | 0 | 1·5 | |
| | 120 | 1·11 | Induction period. |
| | 240 | 0·75 | 5·43 |
| | 360 | 0·51 | 5·41 |
| | 480 | 0·33 | 5·42 |

* $Na_2S_2O_3$ solution equivalent to 1 c.c. of the reaction mixture.

TABLE II

*Effect of varying concentration of potassium oxalate.*

Chloroplatinic acid = 0·01*M*. *R* = conc. of reductant/conc. of oxidant.

| λ. | Conc. of K-bi-oxalate | Intensity abs. (in Einstein). | *R*. | *k*. |
|---|---|---|---|---|
| 436 μμ | 0·105*M* | $9·36 \times 10^{-10}$ | 10·5 | $3·83 \times 10^{-5}$ |
| | 0·06 | 9·38 | 6 | 3·85 |
| | 0 03 | 9·37 | 3 | 3·84 |
| 366 | 0·105 | 4·1 | 10·5 | 5·11 |
| | 0·06 | 4 3 | 6 | 5·12 |
| | 0·03 | 4·2 | 3 | 5·13 |

TABLE III

*Effect of varying the concentration of chloroplatinic acid*

| λ. | K-bioxalate | Chloroplatinic acid | $I_{abs}$. | $k_1$. | *P/Q* |
|---|---|---|---|---|---|
| 436 μμ | 0·07*M* | 0·0133*M* | $11·4 \times 10^{-10}$ | $5 \times 10^{-5}$ | 0·43 |
| | 0 05 | 0·006 | 8 55 | 3·83 | 0·44 |
| 366 | 0·07 | 0·0133 | 2·13 | 2·7 | 1·27 |
| | 0·05 | 0 006 | 1·50 | 1·9 | 1·26 |

TABLE IV

*Effect of varying the intensity of absorbed radiation*

Chloroplatinic acid = 0·01*M*. K-bi-oxalate = 0·07*M*.

| | 436 μμ | | 366 μμ. | |
|---|---|---|---|---|
| $I_{abs} . 10^{10}$ | 13·84 | 7·05 | 4·1 | 1·35 |
| $k_1 \times 10^5$ | 5·75 | 3 22 | 5 0 | 1·7 |
| *P/Q* | 0·41 | 0·44 | 1 22 | 1·26 |

TABLE V

*Determination of quantum efficiency* (γ)

| λ | K-bioxalate | Platinic acid. | $I_{abs}$. | γ. |
|---|---|---|---|---|
| 366 μμ | 0·105*M* | 0·01*M* | 1347 ergs. | 0·84 |
| 436 | 0·105 | 0·01 | 684 | 0·73 |

TABLE VI

*Extinction coefficient of* Pt *complexes and reduced* Pt *complexes.*

| | Mol extinction coefficient (*l*) in. | |
|---|---|---|
| | 366 μμ. | 436 μμ. |
| Pt (ic) complex | 31 | 20 |
| Pt (ous) complex | 10 | 16 |

solution had to be exposed to light for sufficiently long period to get an appreciable amount of reaction. The 50% reduced Pt-complex solution was however examined for any optical activity by exposure to *d*- or *l*-circularly polarised light, but was found to possess none.

The mol. extinction coefficient (Table VI) has been measured by the well known formula $\epsilon.\,c.\,d=\log I_0/I_t$, the terms having the usual significance.

The mechanism of the photochemical process can be put thus—

(*i*) Complex molecule $+h\nu\rightarrow$activated complex. (*ii*) Activated complex→normal complex by spontaneous deactivation of deactivation by collision with solvent molecules. (*iii*) Activated complex→reduced platinous complex and oxidised organic molecule.

Denoting the concentration of activated complex by $c_A$ and that of the organic molecule *i.e.*, reductant by $c_B$, we have, under steady condition, *i.e.*, when $c_A$ does not vary,

$$\frac{I_{abs}}{Nh\nu}=k_2c_A+k_3c_A \quad\text{or}\quad c_A=\frac{I_{abs}}{Nh\nu}/(k_2+k_3)$$

The rate of reaction $$\frac{dx}{dt}=k_3c_A=\frac{k_3}{k_2+k_3}\times\frac{I_{abs}}{Nh\nu}$$

*i.e.*, proportional to the amount of light absorbed by the platinic complex.

Now when 366 $\mu\mu$ is the exciting radiation, it has been observed that the extinction coefficient of the platinous complex is much smaller in comparison to that of the platinic complex, and therefore the velocity of reaction can be written as

$$dx/dt=KI_0(1-e^{-\lambda(a-x)}$$

where $K$ is the proportionality factor and $I_0$, the intensity of incident light. Integrating we get $K\lambda I_0.t=\log.\ \frac{a}{a-x}\ \frac{\lambda.x}{2+\lambda a}$ taking the first term in the expansion.

Here $\lambda$ and $I_0$ remaining constant, as the amount of substance transformed $x$ will gradually increase, the velocity constant as calculated by $1/t\ \log a/a-x$ will gradually decrease. This has been actually observed in these experiments.

But when 436 $\mu\mu$ was the exciting light, though the extinction coefficients of the platinic complex and the platinous complex are smaller in magnitude, they may approximately be taken as equal (*vide* Table VI on extinction coefficient).

$$\text{Here } dI/I=-\left[\frac{\lambda_1(a-x).dy}{l}+\frac{\lambda_2x.dy}{l}\right]$$

where $l$ is the thickness of the cell, $dy$ is the region at which the absorbed radiation is to be measured. Allowing stirring at quick intervals, we have taken the average concentration.

Hence, $$I_{abs}=I_0.\,e^{-\frac{\lambda ay}{l}} \text{ as } \lambda_1=\lambda_2=\lambda \text{ (suppose).}$$

Considering the effective radiation only,

$$dx/dt=K.\int_0^l I_{abs}.\frac{\lambda.(a-x)}{l}.\,dy=K.\frac{a-x}{a} \text{ other factors remaining constant.}$$

$$=K(a-x) \text{ for each experiment.}$$

Here in fact concordant unimolecular constants were obtained. The absence of any optical activity with 50% decomposition of the complex in any one of the two kinds of circularly polarised light may be due to spontaneous racemisation of the active variety formed during the process.

## *The Photochemical Decomposition of the Complex formed between Chloroplatinic Acid and Potassium Malonate.*

*Determination of the Order of a Reaction.*—Here again as in the case of bioxalate with blue light the reactions follow unimolecular course, but in ultraviolet light the unimolecular velocity constants decrease slightly with time. The unimolecular constants record the change for one hour after the induction period is over.

TABLE VII

*Effect of varying the concentration of chloroplatinic acid.*

| λ | Conc. of pot-malonate. | Conc. of chloroplatinic acid. | $I_{abs}$.* | $k_1$. | $P/Q$. |
|---|---|---|---|---|---|
| 366μμ | 0·07*M* | 0·0133*M* | $4·05 \times 10^{-10}$ | $4·72 \times 10^{-5}$ | 1·16 |
| | 0·06 | 0·009 | 3·9 | 4·24 | 1·10 |
| 436μμ | 0·07 | 0·0133 | 2·8 | 0·85 | 0·30 |
| | 0·06 | 0·009 | 2·5 | 0·71 | 0·284 |

* $I_{abs.}$ has been presented in Einstein units

TABLE VIII

*Effect of wave-length of light employed on quantum yield.*

| λ. | Conc. of pot-malonate. | Conc. of chloroplatinic acid. | $I_{abs}$. | $k_1$ | Quantum efficiency. (γ) |
|---|---|---|---|---|---|
| 366μμ | 0·07*M* | 0·0133*M* | $4·05 \times 10^{-10}$ | $4·72 \times 10^{-5}$ | 4·02 |
| 436μμ | ,, | ,, | 4·106 | 0·86 | 1·16 |

As the concentration of chloroplatinic acid is increased, the amount of absorbed radiation and the velocity constant also go on increasing.

TABLE IX

*Effect of varying the intensity of absorbed radiation.*

Malonate = 0·07*M*. Chloroplatinic acid = 0·0133*M*.

| | 0·366μμ | | 436μμ. | | |
|---|---|---|---|---|---|
| $I_{abs}$ (Einstein × $10^{10}$) | 4·05 | 2·94 | 4·11 | 3·04 | 2·47 |
| Velocity const. ($k_1 \times 10^5$) | 4·72 | 2·92 | 0·87 | 0·62 | 0·51 |

The rate of reaction is thus proportional to the intensity of absorbed radiation.

TABLE X

*Effect of varying the potassium malonate to chloroplatinic acid ratio (=R).*

Temp. = 30°.

| | λ = 366 μμ ; $I_{abs.} = 3·85 \times 10^{-10}$ | | | λ = 436 μμ ; $I_{abs.} = 2·65 \times 10^{-10}$ | | |
|---|---|---|---|---|---|---|
| Malonate. | 0·12*M* | 0·06 | 0·03 | 0·12 | 0·06 | 0·03 |
| *R* | 12 | 6 | 3 | 12 | 6 | 3 |
| $k_1$ | $3·86 \times 10^{-5}$ | 3·84 | 0·77 | 0·83 | 0·82 | 0·17 |
| γ (for first hour) | 3·8 | 3·5 | 0·65 | 1·6 | 1·4 | 0·3 |

Up to a limit the variation of concentration of reductant has slight effect upon the velocity of reaction. Beyond this limit the decrease in concentration of the reductant brings about an abrupt drop in the velocity of reaction. The amount of light absorbed remained almost the same in all these cases.

*Effect of Polarised Light.*—The results obtained were the same as with potassium oxalate. The 50% reduced potassium complex solution, reduced by exposing it to *d*- or *l*-circularly polarised light, was tested for any optical activity with negative result only.

## DISCUSSION

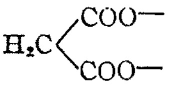
The influence of the concentration ratio of potassium malonate/ chloroplatinic acid $(=R)$ is interesting in this reaction. When the ratio $R$ is about 3, the quantum yield of the process is about unity. But when $R$ is slightly above 3, quantum yield jumps up to a much higher value and is about 4 when $R=6$, though the absorption of energy does not change.

The reaction is attended with no induction period so long as the ratio $R$ is 3, but with higher values of $R$ induction period suddenly appears and goes on increasing with increasing values of $R$.

The characteristics mentioned above can be explained in the same manner as in the previous section.

In fact the central feature of this reaction is the peculiar influence of the ratio $R$ on induction period, velocity and quantum yield. These peculiarities can be explained in the following way.

(*i*) $R=3$. Chloroplatinic acid with three times its concentrations of potassium malonate forms a complex of the type $H_2Pt\,(M'')_3$, when $M''$ stands for $H_2C\begin{smallmatrix}COO- \\ COO-\end{smallmatrix}$



On exposure to light this complex decomposes according to the scheme:

$$H_2Pt(M'')_3 + h\nu \longrightarrow H_2Pt(M'')_3 \text{ (active)}.$$

$$H_2Pt(M'')_3 \text{ (active)} \longrightarrow H_2Pt(M'') + \text{oxidised organic molecule}.$$

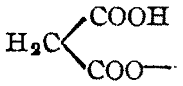
Here the compound $H_2Pt(M'')_3$ has with E.A.N.* $=86$, the stable structure of inert radon. Simultaneous release of two electrons by simultaneous detachment of two covalent bonds, due to splitting off of one $M''$, establishes a stable structure.

The quantum yield in this case ought to be unity. Experimental evidence supports this expectation.

(*ii*) $R>3$. The rate of reaction is entirely different and suggests that some other complex may be involved in the reaction.

For the secondary ionisation constant of malonic acid

$$\frac{[H^{\cdot}]\times[M'']}{[HM']}=K, \text{ where } K=1\times10^{-6} \text{ and } HM'\equiv H_2C\begin{smallmatrix}COOH \\ COO-\end{smallmatrix}$$



In our reaction mixture $H^{\cdot}$ concentration $=$ approximately $10^{-4}N$.

Hence, $$\frac{[M'']}{[HM']}=1\times10^{-2}$$

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* E.A.N. stands for effective atomic number. Atomic number of platinum is 78. Formation of six co-valent bonds with $3M''$ ions results in the sharing of 6 more electrons. Two more electrons are available from two hydrogen atoms. So E.A.N. for $H_2Pt(M'')_3$ is $78+6+2=86$.

When $R=3$, practically all the $M''$ ions are taken up by the complex. So the concentration of $HM'$ is negligible. Hence the chance of formation of any complex of the type $H_2Pt(HM')_6$ is small. When $R > 3$, there is some free $M''$ in the solution and in consequence there must be some $HM'$ ions also. In this case the complex $H_2Pt(HM')_6$ is formed. As the formation of this complex removes free $HM'$ ions from the solution more $HM'$ ions are formed to keep up the equilibrium.

This complex decomposes photochemically according to the scheme :—

(*i*) $H_2Pt(HM')_6 + h\nu \longrightarrow H_2Pt(HM')_6$ (active).

(*ii*) $H_2Pt(HM')_6(\text{active}) + H_2Pt(HM')_6 \longrightarrow 2H_2Pt(HM')_5 + CO_2$ + other products of oxidation of malonic acid.

The complex $H_2Pt(HM')_5$ is with unstable E.A.N. 85, and is very active because it possesses one lone unshared electron and it takes part in further reactions thus :—

(*iii*) $2\{H_2Pt(HM')_5 + H_2Pt(HM')_6\} \longrightarrow 4H_2Pt(HM')_4 + 6CO_2$ and other products of oxidation of malonic acid.

The complex $H_2Pt(HM')_4$ with E.A.N. 84, has two unshared electrons which mutually establish a stable structure.

The mechanism indicates a quantum yield of 4. In our experimental results quantum yield of this reaction is nearly 4, when the ratio $R$ is above 3, specially when $R$ is 6.

The sudden appearance of the period of induction when the ratio $R$ is raised slightly above 3, and also its increase with the increase of $R$, can be explained in a qualitative way on similar considerations assuming that the complex $H_2Pt(HM')_6$ is not formed in the dark. When the reaction mixture is exposed to light, the trimalonate compound, formed in the dark, first of all changes to a complex with higher number of malonate radicals. The time taken for such transformation before the actual photo-decomposition can begin, appears as induction period. Again, the higher the excess malonate present, the higher will be the extent of such transformation. So the induction period will also increase with $R$.

Here also the absence of any optical activity in the reaction mixture after 50% decomposition under the action of polarised light indicates the possibility of some process of racemisation occurring along with the photo-decomposition.

It must be noted here that the stability of the ring formed between the metallic ion and malonic radical, which is responsible for the existence of asymmetric structure of the complex molecule is much less than the corresponding oxalate compound as evident from the experimental results. This also diminishes the chance of obtaining optical activity in the reaction mixture by favouring racemisation.

Our best thanks are due to Sir J. C. Ghosh and Prof. S. N. Bose for their kind interest in this piece of investigation.

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# HYDRIDES OF NICKEL

By Rai Bageshwari Nath Sahai and R. C. Ray

A method for preparing nickel hydride in fairly large quantities has been described. It has been found that between 0° and 150° only two hydrides of nickel, $NiH_2$ and NiH, exist. Decomposition pressures of $NiH_2$ has been determined from room temperature to 150°. The heat of formation of $NiH_2$, calculated from the decomposition pressures, shows that it is of the same order of magnitude as those of the alkali and alkaline earth metals.

In a series of papers Weichselfelder and co-workers (Schlenk and Weichselfelder, *Ber.*, 1923, **56 B**, 2030; Weichselfelder and Thiede, *Annalen*, 1926, **447**, 64; Weichselfelder and Kossodo, *Ber.*, 1929, **62 B**, 769) described the action of passing dry hydrogen into a solution of phenyl magnesium bromide in dry ether in which powdered anhydrous nickel chloride was suspended. They came to the conclusion that a hydride of nickel of the formula $NiH_2$ was formed according to the equation :

$$NiCl_2 + 2\ PhMgBr + 2H_2 = NiH_2 + 2\ C_6H_6 + MgBr_2 + MgCl_2$$

$NiPh_2$ is said to be formed as an intermediate product which decomposes into $NiH_2$ and $C_6H_6$ under the influence of hydrogen. According to Balandin, Erofeev, Pecherskaya and Stakhanova (*J. Gen. Chem. U.S.S.R.*, 1941, **11**,577), however, PhMgBr reduces nickel chloride to metallic nickel and the colloidal nickel thus formed absorbs hydrogen to form NiH, $NiH_2$ and $NiH_4$ depending upon the quantity of hydrogen taken up : $NiCl_2 + 2PhMgBr + 2H_2 = NiH_4 + Ph_2 + MgBr_2 + MgCl_2$. The present investigation was started with a view to finding out, if only one definite hydride or several hydrides were formed, and also the nature of these hydrides.

Weichselfelder and his collaborators (*loc. cit.*) obtained the hydride in minute quantities and carried out its analysis *in situ*. As it was intended to prepare larger quantities of the hydride the apparatus shown in Fig. 1 was used. **A** was a round-bottomed flask with short neck. It was provided with a rubber bung, **B**, through which passed a glass stirrer, **C**, a dropping funnel, **D**, and inlet and outlet tubes, **E** and **F**, for hydrogen. Perfectly anhydrous and finely powdered nickel chloride was added to the dry ether in **A** and a stream of hydrogen, purified by passing through a mixture of dichromate and concentrated sulphuric acid, over heated copper and finally through concentrated sulphuric acid, was passed into the flask. The nickel chloride was constantly agitated by means of **C**. When all air had been displaced, the solution of freshly prepared PhMgBr in dry either in **D** was run in. The phenyl magnesium bromide must be freshly prepared otherwise the reaction does not take place satisfactorily. For every gram of nickel chloride, 100 c.c. of dry ether were put into **A** and 50 c.c. of ethereal solution of PhMgBr containing 0·1 mol. of magnesium was used for the reaction. As soon as PhMgBr was introduced, the colour of the suspension began to change and finally it became black. The reaction was complete in 3 to 4 hours.

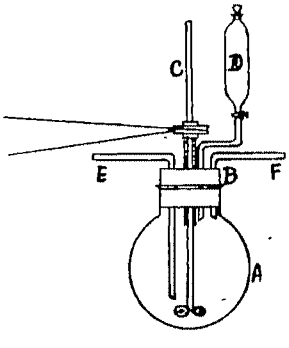

Fig. 1.

If nickel hydrides were merely adsorption compounds, as stated by the Russian workers, it was likely that compounds of different compositions would form when the preparation was made at different temperatures and hydrogen was passed for different periods. With a view to testing this point, the preparations were carried out at, 0°, 15° and 25° by immersing the reaction flask in a suitable bath maintained at these temperatures and in some cases hydrogen was passed for a long time even after the reaction was complete. When the experiment was over, a small quantity of the substance was removed and its composition determined in the following manner. As the hydride is quantitatively decomposed into metallic nickel and hydrogen by water or alcohol, the small quantity of the substance taken out was introduced into a small flask fitted with a dropping funnel and a delivery tube, which was connected to a Hempel's burette. A measured volume of water-alcohol mixture was introduced through the dropping funnel and the evolved gas was collected in the burette. The decomposition occurred rapidly and the volume of hydrogen evolved was obtained by subtracting the volume of the liquid introduced from the total volume of gas collected. The nickel was then dissolved in the flask by adding dilute sulphuric acid and the nickel estimated in the solution as the nickel salt of dimethylglyoxime. It was found that volume of hydrogen evolved on the addition of acid was always equal to that given out on the addition of water. A large number of preparations was made at each temperature and the product obtained in each case was analysed and the results agreed quite closely. One typical result for each temperature is recorded in Table I.

TABLE I

| Temp of preparation. | Wt. of Ni | Vol. of $H_2$ (N.T.P ) | Composition. |
|---|---|---|---|
| 0° | 0·1863 g. | 69 0 c.c. | $NiH_2$ |
| 15° | 0·4512 | 171·8 | $NiH_2$ |
| 25° | 0·2792 | 102·0 | $NiH_2$ |

The decomposition pressures of the hydride were determined at different temperatures. For this purpose the hydride was repeatedly washed by decantation with dry ether and finally filtered through Allhin's apparatus in an atmosphere of hydrogen. The filtered substance was then dried by putting it in a test-tube through which a current of dry hydrogen was passed for some hours. The test-tube was kept immersed in a water-bath at 25°. The substance finally obtained was perfectly dry but still contained traces of magnesium salts as impurities. Measurements of decomposition pressures were repeated in four separate experiments with different samples of the hydride, and as the results were reproducible within 2 mm., it was clear that the presence of traces of impurities in the hydride did not vitiate the results to any great extent.

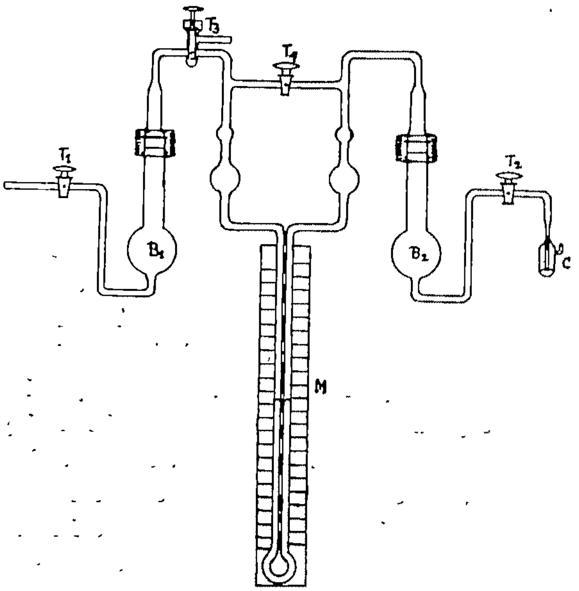

FIG. 2.

The all-glass apparatus used for measurements of pressure is shown in Fig. 2. The apparatus was so constructed that the volume of the apparatus from tap $T_1$ to tap $T_4$ and the mercury level in the manometer **M** on the left-hand side is equal to that from tap $T_2$ to $T_4$ and the mercury level in the manometer on the right-hand side. In order to test that the volumes on the two sides were actually the same, the air inside the apparatus was completely displaced by pure and dry hydrogen which was introduced through $T_1$ and allowed to go out through the mercury trap **C**. The gas was passed for sometime with $T_4$ open and sometime with $T_4$ closed. When $T_4$ was closed the gas passed through **M** pushing up the mercury into the small bulbs above. When the apparatus had been filled with hydrogen, $T_1$ and $T_2$ were closed, and pressure of gas on the two limbs was equalised by opening $T_4$ which was then closed.

The apparatus was put into an electrically maintained air thermostat which could be kept constant to ±0·1°. The thermostat was maintained at different temperatures and no change in the levels of mercury in **M** was noticeable indicating equal volumes.

For measurement of the decomposition pressures, a small quantity of dry nickel hydride, in a small weighing tube was introduced into $B_1$, the whole apparatus from the three-way tap $T_3$ remaining filled with hydrogen. The air in $B_1$ was displaced by dry hydrogen which was introduced through **T** and allowed to escape through the other opening of $T_3$. Gas pressure on the two sides was equalised through $T_4$. The thermostat was set at definite temperatures, and at each temperature it was kept for sufficiently long time until equilibrium was attained. At each temperature the heights of mercury in the two arms of the manometer were read off by means of a cathetometer provided with a vertical scale and vernier. The difference between the heights gave the pressure at each temperature. The mean values of three different sets of experiments are recorded in Table II.

TABLE II

| Temperature ... | 29·8° | 41·2° | 51·2° | 63·8° | 70·2° | 81° | 89° | 110·2° | 130° | 149·6° |
|---|---|---|---|---|---|---|---|---|---|---|
| Pressure (m.m.) ... | 10·0 | 32·0 | 52·0 | 89·0 | 112·0 | 149·5 | 174·8 | 248·0 | 317·0 | 384·0 |

The above results are plotted in Fig. 3. It will be observed that it consists of two straight lines which intersect sharply at one point indicating the presence of two solid phases. The point of intersection which occurs at 56° is the transition temperature of one form into the other. The change is irreversible, because it has been found that when the substance, which is formed at higher temperatures, is cooled to the room temperature in contact with hydrogen and left for 48 hours, hydrogen is not reabsorbed. The composition of the second solid phase has been determined by analysis. For this purpose the dihydride was heated to different temperatures from 70° to 150° and allowed to cool in contact with the evolved hydrogen, the ratios of hydrogen to nickel in the products were determined. The volume of hydrogen evolved when decomposed by the action of dilute sulphuric acid was collected and measured and the nickel in the solution was estimated by dimethyl glyoxime. The results obtained are tabulated below.

FIG. 3

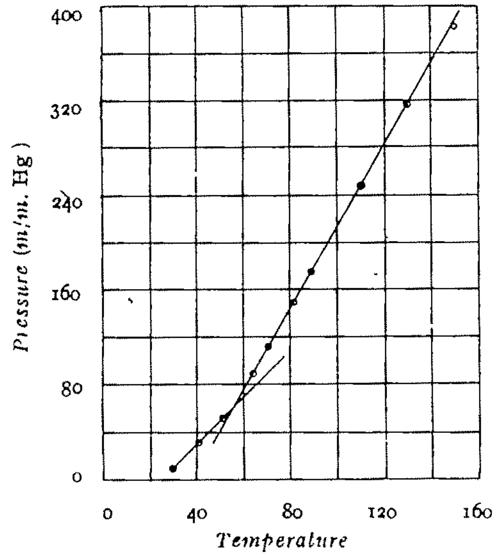

TABLE III

| Temp. of bath. | Vol. of hydrogen at N. T. P. | Wt. of Ni. | Composition |
|---|---|---|---|
| 70° | 22·6 c.c. | 0·1110 g | NiH |
| 100° | 27·2 | 0·1480 | NiH |
| 130° | 26·3 | 0·1410 | NiH |
| 150° | 25·7 | 0·1347 | NiH |

Nickel dihydride is a spongy, black substance which is fairly stable when kept under ether at temperatures below 0°. It decomposes rapidly in contact with moist air but in dry air the rate of decomposition is slow even at the ordinary temperature. It is decomposed quantitatively by water, alcohol or dilute acids; with the first two the decompsition is catalytic in nature resulting in the separation of metallic nickel and only two atoms of hydrogen are evolved per molecule of the hydride but with acids, the nickel salt of the acid is formed and four atoms of hydrogen are given out per molecule of the hydride. The formation of the hydride takes place mainly according to the equation given by Weichselfelder (*loc. cit.*) but it seems sometimes traces of diphenyl are also produced. Nickel monohydride has a slightly crystalline appearance, and is comparatively stable than the dihydride. It is completely decomposed by dilute acids. No evidence of the formation of $NiH_4$ has been found, although reactions were carried out at temperatures ranging from 0° to 25° and by passing hydrogen for varying lengths of time.

It is possible to calculate the heat of formation from the decomposition pressure-temperature data by means of the following thermodynamic relation, which is derived from the well known Clapeyron-Clausius equation,

$$\frac{d \log p}{dT}=\frac{Q}{RT^2} \text{ which, on integration, gives } Q=\frac{RT_1T_2}{T_2-T_1}\log\frac{p_2}{p_1}$$

where $Q$ = heat of formation, $R$ = 1·9885 cal. and $p_1$ and $p_2$ are the decomposition pressures at temperatures $T_1$ and $T_2$ respectively. The above equation can be used with exactness only at low pressures and small variations of temperature. While the importance of directly measured heat data is not denied, the calculated values are, no doubt, fair approximations to, or at least, capable of indicating the order of, the correct values. The heats of formations calculated in this manner are recorded in the following table.

TABLE IV

| | Substance = $NiH_2$ | | | Substance = NiH | | |
|---|---|---|---|---|---|---|
| Temperature | 35·5° | 40·5° | 46·2° | 67° | 75·6° | 85° |
| Heat of formation (cal.) ... | 19,330 | 15,060 | 9,971 | 8,264 | 6,472 | 4,968 |

The heat data recorded in literature are usually for a temperature of about 18°. The heat of formation $Q_2$ at temperature $T_2$ may be calculated from the equation

$$Q_2=Q_1+C_p(T_2-T_1)$$

in which $Q_1$ is the heat of formation at temperature $T_1$ and $C_p$ is the molecular heat capacity. The values of $C_p$ for the hydrides $NiH_2$ and NiH are not known at any temperature. Over a small range of temperature the values of $C_p$ may be regarded as constant, so that if the heat data are plotted against the temperatures, straight lines are obtained. When these lines are exterpolated to 18°, the value of heat of formation of $NiH_2$ comes out as 35,200 cals. and that of $NiH$ as 17,100 cal. The heat of formation of $NiH_2$ is thus comparable in magnitude with heat of the salt-like hydride $BaH_2$ for which the recorded value is 40,960. The high values of the heats of formation of the nickel hydrides suggest that there can be little distinction in the type of chemical binding in these compounds with that of the hydrides of alkali and alkaline earth metals. From the method of their preparation, there appears to be no analogy of nickel hydrides with such substances as the rare earth hydrides, nor is there any reason to suppose that these bear any relation with the products obtained when finely divided nickel absorbs hydrogen.

Further work on these type of compounds are in progress In conclusion we wish to record our thanks to Dr. P. B. Ganguly and Mr. P. C. Sinha for their kind interest and ungrudging help

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# CHARGE AND STABILITY OF COLLOIDS. PART V. POTENTIOMETRIC TITRATIONS OF CHROMIUM HYDROXIDE SOL

By B. P. Yadava

In this paper the release of chlorine ions from the counter part of the double layer in $Cr_2O_3$ sols, prepared by adding ammonia to $CrCl_3$, has been studied by the slow potentiometric titration method. It has been found that the amount of chlorine released from the $Cr_2O_3$ sol like that of $Fe_2O_3$ and $Al_2O_3$ sols depends on the purity of the sol.

A theoretical explanation for the super-equivalent release of the chlorine, based on the electrical adsorption of these ions on the surface of the colloidal particles of the hydrous oxide sols, has been advanced.

In previous communications of this series (*J. Indian Chem. Soc.*, 1943, **20**, 25, 110, 115, 120) it has been shown that super-equivalent amount of chlorine is displaced from ferric hydroxide and aluminium hydroxide hydrosols on the addition of multivalent coagulating ions when the sols are not sufficiently pure. With the progress of dialysis and the consequent increase in purity a point is reached after which an amount of chlorine less than the added electrolyte is released from both the above mentioned sols.

In this paper chromium hydroxide hydrosols, prepared by the addition of ammonia to chromium chloride is studied. The displacement of chlorine ions from the counter part of the double layer is measured potentiometrically as in the previous papers (*loc. cit.*) by an arrangement similar to that adopted by Weiser (*J. Phys. Chem.*, 1943, **35**, 1).

## EXPERIMENTAL

The experimental procedure followed in this paper is just the same as described in the previous communications of this series of papers (*loc. cit.*). The chromium hydroxide sol was prepared by taking about 80 g. of chromium chloride and dissolving it in freshly prepared distilled water and diluting the solution to about 4 litres. Dilute ammonia was added drop by drop followed by thorough shaking of the solution after each addition of drop of ammonia till the sol was just short of precipitation. The solution was left overnight and filtered the next morning. A small portion of the solution was kept aside for potentiometric titrations with the undialysed sol and the rest was kept for progressive dialysis in two Neidle dialysers. Samples of the sol at different purity were taken out from the dialysers after every sixth day and each sample titrated by step-wise addition of the electrolytes. The results obtained have been given in the following tables and shown graphically in Fig. 1. To economise space only two tables are given. Seven different samples of the sol have been titrated with $KNO_3$, $K_2SO_4$, and K-citrate but results with two sols only are recorded.

## DISCUSSION

From the tables given below it is clear that $Cr_2O_3$ sol also behaves in a manner similar to those of $Fe_2O_3$ and $Al_2O_3$ sols (*vide* previous publications, *loc. cit.*).

### TABLE I

### *Sol* III.

$Cr_2O_3$ sol = 6·01 g./litre. Chlorine = 0·0643 g. ions/litre. Purity* of the sol = 93·49. Temp. = 25°.

| | π. | $a_{cl}$ | Chlorine × $10^3$ | | |
|---|---|---|---|---|---|
| | | | Total. | Displaced | Equiv. to ppt ion added. |
| | | | $KNO_3$ (*N*) | | |
| 0·00 c.c | 0·0403 volts | 16·52 × $10^{-3}$ | 18·42 | 0·00 | 0·00 |
| 2·00 | 0·0328 | 22·13 | 25·26 | 6·84 | 100·00 |
| 5·00 | 0·0310 | 23·74 | 27·19 | 8·77 | 250·00 |
| 7·00 | 0·0306 | 24·12 | 27·69 | 9·27 | 350·00 |
| | | | $K_2SO_4$ (*N*/20) | | |
| 1·00 | 0·0369 | 18·87 | 21·15 | 2·73 | 2·50 |
| 2·00 | 0·0335 | 21·54 | 24·32 | 5·90 | 5·00 |
| 3·50 | 0·0294 | 25·28 | 28·92 | 10·50 | 8·75 |
| 5·50 | 0·0266 | 28·18 | 32·54 | 14·12 | 13·75 |
| | | | K-citrate (*N*/50) | | |
| 2·00 | 0·0368 | 18·94 | 21·25 | 2·83 | 2·00 |
| 4·00 | 0·0348 | 20·48 | 20·09 | 4·67 | 4·00 |
| 6·00 | 0·0329 | 22·05 | 25·00 | 6·58 | 6·00 |
| 8·00 | 0·0294 | 25·28 | 28·88 | 10·46 | 8·00 |

### TABLE II

### *Sol* IV

$Cr_2O_3$ sol = 5·83 g./litre. Chlorine = 0·0361 g. ions/litre. Purity* of the sol = 161·50. Temp. = 25°.

| | π. | $a_{cl}$. | Chlorine × $10^{-3}$ | | |
|---|---|---|---|---|---|
| | | | Total | Displaced. | Equiv. to ppt ion added |
| | | | $KNO_3$ (*N*) | | |
| 0·00 | 0·0571 volts | 8·59 × $10^{-3}$ | 9·38 | 0·00 | 0·00 |
| 2·00 | 0·0480 | 12·25 | 23·52 | 4·14 | 100·00 |
| 4·00 | 0·0460 | 13·24 | 14·67 | 5·29 | 200·00 |
| 6·00 | 0·0454 | 13·55 | 15·06 | 5·68 | 300·00 |
| | | | $K_2SO_4$ (*N*/20) | | |
| 1·00 | 0·0513 | 10·77 | 11·87 | 2·46 | 2·50 |
| 2·00 | 0·0479 | 12·30 | 13·57 | 4·19 | 5·00 |
| 3·50 | 0·0430 | 14·87 | 16·53 | 7·15 | 8·75 |
| | | | K-citrate (*N*/50) | | |
| 2·00 | 0·0539 | 9·73 | 10·66 | 1·28 | 2·00 |
| 5·00 | 0·0470 | 12·73 | 14·09 | 4·71 | 5·00 |
| 7·00 | 0·0452 | 13·66 | 15·16 | 5·78 | 7·00 |

* Purity of the sol in the tables refers to the ratio of $Cr_2O_3$ to chlorine content of the sol

The following table gives the relation between purity and chlorine displaced from $Cr_2O_3$ sol as used herein.

### TABLE III

| Sol. | Conc of sol per litre | Chlorine content of the sol per litre | $\frac{Cr_2O_3}{Cl}$ | Nature of displacement of Cl |
|---|---|---|---|---|
| I | 6·78 g | 0·2155 g ions | 31·46 | Super equiv. |
| II | 6·16 | 0·1197 | 51·46 | ,, |
| III | 6·01 | 0·0643 | 93·49 | ,, |
| IV | 5·83 | 0·0361 | 161·50 | Less than equiv. |
| V | 5·64 | 0·0214 | 263·50 | ,, |
| VI | 5·58 | 0·0132 | 422·10 | ,, |
| VII | 5·52 | 0·0099 | 557·50 | ,, |

From this it is clear that the same sol begins to release less Cl than equivalent of electrolyte added as soon as its purity reaches a certain point.

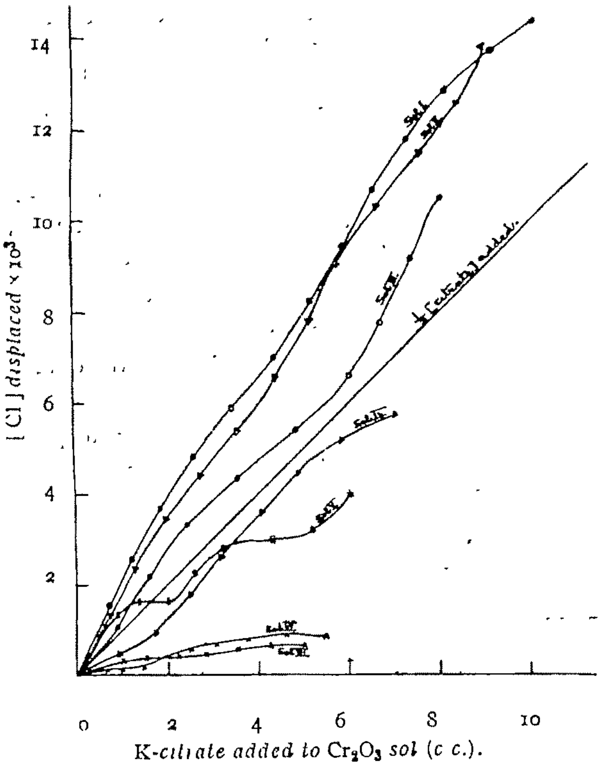
### *Super-equivalent Displacement of Chlorine Ions*

In order to explain the super-equivalent release of chlorine ions on coagulation of the sol it is necessary to bear in mind that such release of Cl ions is associated with the presence of considerable amount of the impurity in the inter-micellary liquid. On account of this, Cl is present in such a form as not to be determinable potentiometrically. On neutralisation of the charge on the colloid this osmotically inactive Cl becomes active. This inactive chlorine is different from the fixed Cl which constitutes the rigid portion of the outer part of the double layer. The Cl ions from the rigid portion of the counter ions can in no account be more than what is equivalent to the total charge on the colloidal particle and which is measured by the amount of the coagulating ion added to the sol provided it is completely adsorbed by the sol. But since an amount of Cl, super-equivalent to the added polyvalent coagulating ions is released it is certain that fixed chlorine is in two different states *i.e.*, one which constitutes the rigid portion of the counter part of the double layer, and the other which is present on the surface of the colloid as ion pairs. This means that the surface of the colloidal particle contains both positive and negative ions as ion pairs, a part of which is ionised to give an effective positive charge to the surface.

On the basis of the above observations a mechanism of coagulation is suggested below which explains the super-equivalent release of chlorine ions from the hydrous oxide sols.

### *Mechanism of Coagulation of Hydrous Oxide Sols*

From the foregoing results it appears that when, say, the $Fe_2O_3$ sol is impure, the surface of the colloid is covered with $Fe^{\cdot\cdot\cdot}$ and $H^{\cdot}$ ions as the primary adsorbed ions to give an effective positive charge to the colloid, and also with ion pairs such as Fe and Cl as well as H and Cl ions. With progress of dialysis the electrically adsorbed ions forming the unionised ion pairs are ionised due to the washing away of chlorine ions from the surface and thus the positively charged ions are left on the surface and so the charge on the surface continually increases. This is supported by the experimental results of Mukherjee, Chaudhury and Ghosh (*Trans. Nat. Inst. Sci. India*, 1935, **1**, 47) and Desai and Borker (*Trans. Faraday Soc.*, 1923, **29**, 1269). Thus with progressively pure sols the quantity of chlorine held on the surface as unionised ion pairs decreases. Hence the amount of super-equivalent release of chlorine ions becomes less and less as the intermicellary liquid becomes purer and purer, as is shown by the general form of the curves in Fig 1.



K-citrate added to $Cr_2O_3$ sol (c c.).

The mechanism of coagulation of the hydrous oxide sols on the addition of electrolytes can also have an explanation in the light of the above considerations :

On addition of electrolytes to the less pure sols a super-equivalent release of Cl ions has been observed. Evidently the coagulating ion, when it penetrates the double layer displaces some chlorine ions from its outer part and this at the best can be equivalent to the amount of the polyvalent ion added provided it is completely adsorbed. In addition to this, as the coagulating ion penetrates the double layer and reaches near enough the surface the charge density on the surface is reduced and thus the electrically adsorbed ions, which were held on the surface of the micelle, are released now owing to low surface density. This produces a super-equivalent release of Cl ions. When, however, the Cl ions, which were electrically held on the surface, are released, the surface should become more positively charged. This view is corroborated from the experimental results of Rabinowitsch and Fodimann (*Z. physikal. Chem.*, 1932, **159**, 403), who observed an increase in the cataphoretic speed of the particles of a sol which displaced super-equivalent amount of Cl ions, on the addition of 0·5*N*-$Na_2SO_4$ solution to $Fe_2O_3$ sol.

With the progress of dialysis the possibility of getting more Cl ions from the surface of the micelle becomes less, because, as the sol is dialysed the surface becomes more and more free from the ion pairs and thus the release of the Cl ions from the electrically held ion pairs on the surface becomes less and therefore at a certain stage of dialysis the super-equivalent release of Cl ions from the micelles on the addition of polyvalent electrolytes ceases and Cl released after that critical stage of dialysis of the sol is always less than the equivalent of the electrolytes added to the sol.

At that stage of dialysis, where the super-equivalent release of Cl ions ceases, one cannot say that the surface of the colloid has been completely freed from the unionised ion pairs. There may be some of the ion pairs still left on the surface and may be sparsely situated and may be comparatively very few in number when compared with the surface of the less pure sols. On addition of electrolytes these ion pairs lose their Cl ions and thus instead of being held in pairs are now left alone on the surface and thus impart a positive charge to the sol. This is supported by the data of Rabinowitsch and Fodimann (*loc. cit*) from the observed increase in the cataphoretic speed of the particles of $Fe_2O_3$ sol which displaced Cl less than the equivalent of the added electrolyte.

In spite of this extra-release of the Cl ions, the possibility of which is not completely debarred, super-equivalent release of Cl does not occur as the quantity of electrically held Cl, which is released from the surface, is small and is probably less than the amount of Cl present in the diffused portion of the outer component of the double layer. So, although there may be an increase in the surface density due to release of comparatively small electrically held Cl ions on the surface, this release may not be sufficiently large to make up for that portion of the double layer and are osmotically active.

The increase in the cataphoretic speed of the collodial particles in those sols which displace Cl ions less than the equivalent was very small when compared with the percentage increase with those sols which displace super-equivalent amount of the Cl ions.

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# CHARGE AND STABILITY OF COLLOIDS. PART VI. STUDY OF THE ADSORPTION OF PRECIPITATING AND STABILISING IONS BY $As_2S_3$ AND $Fe(OH)_3$ SOLS AT THEIR COAGULATING CONCENTRATIONS

By B P. Yadava

Simultaneous adsorption of the coagulating ion as well as of the ion carrying the same charge as the colloid has been estimated during the course of coagulation. The coagulation concentrations used during the course of the experiments have been varied with a view to studying the adsorption of the ions at different ranges of the time of coagulation.

Dhar and collaborators (*J. Phys Chem.*, 1924, **28**, 313; 1925, **29**, 434) believe that the amount of adsorption is greater, the lesser the valency of the precipitating ion, whereas Weiser and co-workers (*ibid.*, 1924, **28**, 233; 1925, **29**, 955; 1926, **30**, 20) are of opinion that greater the valency of the precipitating ion, the greater is the adsorption.

From these views an attempt has been made to correlate adsorption with coagulation concentration. According to Dhar (*loc. cit.*) potassium with a low coagulating power is adsorbed in a larger quantity whereas bi-, and trivalent coagulating ions with greater coagulating powers are less adsorbed. This at first sight appears to be a contradiction as ions with greater adsorption have low precipitating power and *vice versa.*

In our opinion the actual amount, say, of a cation adsorbed by any negatively charged sol primarily depends on the amount of the charge that has to be neutralised, evidently $K^{\cdot}$ions required will be three times the number of $Al^{\cdot\cdot\cdot}$ ions. If a quantity of a sol is taken which carries one faraday of electricity, then 39·10 g. of $K^{\cdot}$ions would be needed to neutralise the charge of the sol, whereas only 8·99 g. of $Al^{\cdot\cdot\cdot}$ions will be required Hence if the quantity of a cation adsorbed mainly depends on charge neutralisation then the ratio of the adsorption of K:Al, if expressed in g. for the same quantity of the colloid, would be 39·10 : 8·99. Here it is clear that $K^{\cdot}$ions are certainly more adsorbed when expressed in g. These quantities may be slightly altered due to adsorption by the neutral coagulated particles, but this adsorption is so small that the relative amount adsorbed will not be markedly changed in the course of coagulation experiments, and therefore the ratio of K:Al ions adsorbed, when expressed in g., will always be considerably greater than one.

This is what is exactly meant by Dhar's statement that $K^{\cdot}$ions are more adsorbed than $Al^{\cdot\cdot\cdot}$ions. But the coagulation concentration bears no relation to these because otherwise coagulation would have a direct numerical relation with valency *i.e.*, the concentration necessary to coagulate any sol by mono-, bi-, tri-, and tetra-valent ions should be in the ratio of $1:\frac{1}{2}:\frac{1}{3}:\frac{1}{4}$, but this is not what we find. Instead we get Wetham's law *viz*, $1:x:x^2:x^3$. This increase in the coagulating power in geometrical progression can be explained by the fact that all the ions added at the coagulation concentration are not completely adsorbed.

In the case of univalent ions the percentage adsorbed is exceedingly small whereas with multivalent ions this percentage increases. This can be easily understood because the electrostatic force between the colloidal particle and the coagulating ion increases with valency, and if the adsorption of the coagulating ion is helped by the electrostatic force then the percentage adsorbed should increase because the minimum energy necessary to enable the ion to penetrate the double layer is smaller in polyvalent ions than in monovalent ions. With the increase in percentage of the coagulating ion adsorbed there is bound to be a decrease in the coagulation concentration. Perhaps it is this increase in the percentage adsorbed from the electrolyte which Weiser has in view when he says that greater is the valency of the precipitating ion, the greater is its adsorption.

In this paper both the actual quantity as well as the percentage adsorbed of various coagulating ions by different colloids have been investigated with a view to substantiating the above argument.

## EXPERIMENTAL

$As_2S_3$ and $Fe(OH)_3$ sols were prepared exactly in the same manner as described in Part I of this series of papers (*J. Indian Chem. Soc.*, 1943, **20**, 25). Arsenious sulphide sol has been coagulated by KCl, $BaCl_2$, and $AlCl_3$ and the adsorption of both anions and cations has been determined. Ferric hydroxide sol was coagulated by KCl, $K_2SO_4$, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$; both anions and cations adsorbed have been estimated.

Both the above mentioned sols were coagulated by adding varying concentrations of the particular electrolyte in question. The highest concentration used was that which coagulated the sol in ten minutes, and the lowest was that which coagulated them in 10 to 16 days. The sol-electrolyte mixtures were left in contact till complete coagulation.

100 C.c. of the arsenious sulphide sol were taken in several glass-stoppered bottles of 200 c.c capacity. To one set of these bottles was added *N*-KCl in varying concentrations; the sol and the electrolyte mixtures being always made up to 200 c.c. by adding the requisite volume of distilled water to electrolyte and then mixed. Similarly $BaCl_2(N/20)$ and $AlCl_3(N/100)$ were added to the sol. In the case of ferric hydroxide sol the volume of the sol taken in each bottle was 50 c.c; the total volume of the sol and electrolyte taken being made up to 100 c.c. The estimations of some of the ions were done gravimetrically while in the case of some of them volumetric method was used. For example K, Ba, Al and $SO_4$ were determined by the usual gravimetric methods while chlorine, ferricyanide and ferrocyanide ions were determined by volumetric methods by titrating chlorine against a standard solution of silver nitrate and ferri-, and ferrocyanide ions against a standard solution of potassium permanganate.

*Adsorption of precipitating and stabilising ions by the* $As_2S_3$ *sol*

Sol. conc. = 17·02 g./litre

TABLE I

| *N*-KCl added | Time of coagulation | K actually adsorbed. | % of K adsorbed | K adsorbed to K equiv. of Cl adsorbed. | Cl adsorbed | % of Cl adsorbed as fraction of | |
|---|---|---|---|---|---|---|---|
| | | | | | | Total chlorine | K adsorbed |
| 16·0 | 10 min | 0·0297 g | 4·74 g | 0·01084 | 0·0171 g | 3·01 | 63·49 |
| 15·0 | 2 hrs | 0·0250 | 4·27 | 0·0078 | 0·0156 | 2·91 | 68·82 |
| 14·0 | 12 hrs. | 0·0210 | 3·84 | 0·0179 | 0·0029 | 0·58 | 14·95 |
| 13·0 | 2 days | 0·0184 | 3·62 | 0·0170 | 0·0014 | 0·31 | 7·65 |
| 12·0 | 4 days | 0·0154 | 3·29 | 0·0149 | 0·00044 | 0·01 | 3·18 |
| 11·0 | 7 days | 0·0143 | 3·33 | 0·0139 | 0·00039 | 0·009 | 3·01 |
| 10·0 | 10 days | 0·0111 | 2·84 | 0·0111 | 0·00001 | 0·003 | 0·09 |

TABLE II

| *N*/20-$BaCl_2$ added. | Time of coagulation | Ba actually adsorbed | % of Ba adsorbed | Ba adsorbed to Ba equiv of Cl adsorbed | Cl adsorbed | % of Cl adsorbed as fraction of | |
|---|---|---|---|---|---|---|---|
| | | | | | | Total chlorine. | Ba adsorb |
| 10·0 c c. | 10 min. | 0·0042 g | 12·26 g. | 0·0036 g | 0·00015 g | 0·88 | 13·84 |
| 9·0 | 2 hr | 0·0055 | 18·74 | 0·0049 | 0·00016 | 1·02 | 11·27 |
| 8·0 | 12 | 0·0058 | 21·17 | 0·0051 | 0·00019 | 1·36 | 12·69 |
| 7·0 | 7 days | 0·0057 | 23·62 | 0·0049 | 0·00020 | 1·61 | 13·59 |
| 6·0 | 10 | 0·0060 | 29·18 | 0·0052 | 0·00021 | 1·98 | 13·56 |

### TABLE III

| *N*/100-$AlCl_3$ added. | Time of coagulation | Al actually adsorbed. | % of Al adsorbed | Al-adsorbed to Al equiv of Cl adsorbed | Cl adsorbed | % of Cl adsorbed as fraction of Total chlorine | Al adsorb. |
|---|---|---|---|---|---|---|---|
| 5·0 c.c. | 10 min. | 0·1103 mg. | 24·53 | 0·1085 mg. | 0·0070 mg. | 0·42 | 1·61 |
| 4·5 | 2 hrs. | 0·1240 | 30·66 | 0·1217 | 0·0090 | 0·56 | 1·84 |
| 4·0 | 4 days | 0·1866 | 51·88 | 0·1842 | 0·0095 | 0·68 | 1·29 |
| 3·5 | 8 | 0·2148 | 68·35 | 0·2123 | 0·0097 | 0·79 | 1·14 |
| 3·0 | 16 | 0·2268 | 84·08 | 0·2243 | 0·0099 | 0·94 | 1·11 |

In the following tables the adsorption of the precipitating ion as well as, the stabilising ion has been determined in a ferric hydroxide sol which was dialysed.

### TABLE IV

Conc. $Fe_2O_3$ sol = 5·024 g./litre. Chlorine content of the sol = 1·367 g./litre.

| 2*N*-KCl added | Time of coagulation | Cl actually adsorbed | % of Cl adsorbed | Cl adsorbed to Cl equiv of K adsorbed | K adsorbed | % of K adsorbed as fraction of Total K added | Cl adsorb |
|---|---|---|---|---|---|---|---|
| 28·0 c.c. | 10 min | 0·0996 g | 5·02 | 0·0425 g | 0·0630 g. | 2·88 | 57·34 |
| 27·0 | 2 hrs. | 0·0852 | 4·45 | 0·0649 | 0·0224 | 1·06 | 23·84 |
| 26·0 | 2 days. | 0·0789 | 4·28 | 0·0636 | 0·0169 | 0·83 | 19·42 |
| 25·0 | 7 | 0·0649 | 3·66 | 0·0606 | 0·0047 | 0·24 | 6·57 |

### TABLE V

| *N*/20-$K_2SO_4$ added. | Time of coagulation. | $SO_4$ actually adsorbed | % of $SO_4$ adsorbed. | $SO_4$ adsorbed to $SO_4$ equiv of K adsorbed | K adsorbed. | % of K adsorbed as fraction of Total K ads. | $SO_4$ ads. |
|---|---|---|---|---|---|---|---|
| 10·0 c.c. | 10 min. | 0·0184 g | 76·67 | 0·0181 g. | 0·0002 g. | 1·02 | 1·34 |
| 8·0 | 2 hrs. | 0·0172 | 89·59 | 0·0168 | 0·0003 | 1·93 | 2·14 |
| 7·0 | 2 days | 0·0157 | 93·47 | 0·0152 | 0·0004 | 2·92 | 3·13 |
| 6·0 | 4 months. | No coagulation occurred during this period | | | | | |

### TABLE VI

| $K_3Fe(CN)_6$ (0·006*N*) added. | Time of coagulation | $Fe(CN)_6$ actually adsorbed | % of $Fe(CN)_6$ adsorbed | *FeX-adsorbed to FeX equiv of K ads | K adsorbed | % of K adsorbed as fraction of Total K | FeX ads. |
|---|---|---|---|---|---|---|---|
| 27·5 c.c. | 10 min. | 9·60 mg | 82·4 | 9·57 mg | 0·008 g | 0·12 | 0·15 |
| 25·0 | 2 hrs | 9·62 | 90·8 | 9·58 | 0·012 | 0·20 | 0·225 |
| 22·5 | 2 days | 8·96 | 93·9 | 8·91 | 0·025 | 0·48 | 0·504 |
| 20·0 | 10 days | 8·104 | 95·6 | 8·04 | 0·036 | 0·76 | 0·802 |

### TABLE VII

| $K_4Fe(CN)_6$ 0·004*N*) added | Time of coagulation | $Fe(CN)_6$ actually adsorbed | % of FeX adsorbed. | *FeX adsorbed to FeX equiv of K ads | K adsorbed | % of K adsorbed as fraction of Total K | FeX ads. |
|---|---|---|---|---|---|---|---|
| 22·0 c.c. | 10 min | 8·22 mg. | 88·2 | 8·212 mg | 0·0055 mg | 0·08 | 0·092 |
| 20·0 | 2 hrs | 7·84 | 92·5 | 7·827 | 0·0094 | 0·15 | 0·165 |
| 19·0 | 1 day | 7·71 | 95·8 | 7·686 | 0·0172 | 0·29 | 0·306 |
| 18·0 | 7 days | 7·469 | 97·7 | 7·427 | 0·0304 | 0·54 | 0·559 |

* Where X represents $(CN)_6$

## DISCUSSION

From the results given in column 8 of the above tables, it is clear that the same ion *e.g.*, Cl in the case of $As_2S_3$ sol and K in the case of $Fe_2O_3$ sol is differently adsorbed when different electrolytes are used for coagulation. When we take uni-univalent salts like KCl the percentage adsorption of the ion carrying the same charge as the colloid is considerable, whereas with $BaCl_2$ and $K_2SO_4$ the same ions are much less adsorbed. The adsorption is still less with $AlCl_3$ and $K_3Fe(CN)_6$. Thus there is experimental evidence that with uni-univalent salts, a considerable percentage of the coagulating ion adsorbed is due to the adsorption of similarly charged ion. When the time of coagulation is increased, the percentage of similarly charged ion decreases in the case of uni-univalent salts

If the valency of the coagulating ion is increased the percentage adsorption increases. It also increases when the time of coagulation is increased with multivalent ions but with univalent ions it decreases. This is probably due to the decrease in the adsorption of similarly charged ion with increase of time of coagulation, as evident from the results given in column 7 of the above tables.

From the above tables the ratios of K : Ba : Al adsorbed, when expressed in moles, as well as the ratios of their coagulating concentrations are given for $As_2S_3$, similarly for $Fe(OH)_3$ sol the ratios of Cl : $SO_4$ . $Fe(CN)_6^{III}$ : $Fe(CN)_6^{IV}$ are given in the following tables. While calculating the ratios of the amount adsorbed, the values given in column 5 of the above tables are taken, as they give the amount of the coagulating ion adsorbed minus the adsorption which is equivalent to the adsorption of the ion carrying the same charge as the colloid.

TABLE VIII

$As_2S_3$ *sol.*

| Time of coagulation. | Relative moles adsorbed K. | Ba. | Al. | Relative coagulating conc. K | Ba. | Al. |
|---|---|---|---|---|---|---|
| 10 min | 68 9 | 6·5 | 1 | 320·0 | 10 | 1 |
| 2 hrs. | 44 2 | 7 9 | 1 | 333 3 | 10 | 1 |
| 12 hrs | 66 9 | 5 4 | 1 | 350 0 | 10 | 1 |
| 7 days | 45 2 | 4 5 | 1 | 314·0 | 10 | 1 |
| 10 days | 34 1 | 4·55 | 1 | 333·3 | 10 | 1 |

TABLE IX

$Fe(OH)_3$ *sol.*

| Time of coagulation | Relative moles adsorbed. Cl. | $SO_4$ | $\overset{III}{Fe(CN)_6}$. | $\overset{IV}{Fe(CN)_6}$. | Relative coagulating conc Cl. | $SO_4$. | $\overset{III}{Fe(CN)_6}$. | $\overset{IV}{Fe(CN)_6}$ |
|---|---|---|---|---|---|---|---|---|
| 10 min. | 30·9 | 4·98 | 1·16 | 1 | 621·9 | 5·68 | 1 875 | 1 |
| 2 hrs | 49 55 | 4·73 | 1·22 | 1 | 675 0 | 5·00 | 1 875 | 1 |
| 2 days | 49 46 | 4·36 | 1 16 | 1 | 684·2 | 4·60 | 1 776 | 1 |
| 7 days | 48 77 | 6 | 1·08 | 1 | 694 5 | 4·167 | 1·667 | 1 |

From the above tables it is clear that the coagulating ions with lesser valency are adsorbed more. Moreover, the ratios are very different from 3 1·5 : 1 for K : Ba : Al in the case of $As_2S_3$ sol, whereas in the case of $Fe(OH)_3$ sol we observe that the ratios of Cl. $SO_4$ : $Fe(CN)_6^{III}$ : $Fe(CN)_6^{IV}$ are far different from 4:2.1·33:1, which we should get if adsorption was only due to charge neutralisation. These results are in complete agreement with the work of Dhar and collaborators.

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# PERIODATES OF COBALT AND NICKEL

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Cobalt sulphate and cobalt nitrate form an iodate of the composition $3CoO_2$, $Co(IO_3)_2$, $10H_2O$ and a new periodate, cobalt diorthoperiodate, $Co_4I_2O_{11}$, $12H_2O$ with disodium paraperiodate and potassium metaperiodate respectively.

Nickel sulphate and nickel chloride form nickel paraperiodate, $Ni_5(IO_6)_2$, 13 $H_2O$ and another periodate of the composition, 7 NiO, $2I_2O_7$, $25H_2O$, with disodium paraperiodate and potassium metaperiodate respectively.

Lautsch (*J. prakt. Chem.*, 1862, **100**, 89) obtained a greenish yellow powder of the composition corresponding to 7 CoO, 2 $I_2O_7$, by evaporating a solution of disodium paraperiodate with an excess of cobalt sulphate. Rammelsberg (*Ber*, 1868, **1**, 70 ; *Pogg. Ann.*, 1868, **134**, 514, 528) failed to prepare a periodate by the above method, but always obtained a mixture of oxide and an iodate.

In order to elucidate the above discrepancy, the action of disodium paraperiodate on cobalt sulphate was studied and it was found that a greenish brown iodate of the composition, $3CoO_2$, $Co(IO_3)_2$, $10H_2O$ was obtained. The analyses of the different samples showed it to be of a constant and reproducible composition, therefore it could not be regarded as a mixture of oxide and iodate, as reported by Rammelsberg (*loc. cit.*).

A new periodate of cobalt, cobalt diorthoperiodate, $Co_4I_2O_{11}$, $12H_2O$, was obtained by the action of a hot solution of potassium metaperiodate on a solution of cobalt nitrate. The precipitates obtained in both the cases were washed with water and dried in an air-oven at 45°.

## EXPERIMENTAL

The analyses of the salts were carried out by estimating (*i*) cobalt by the electrolytic method (Scott, "Standard Methods of Chemical Analysis", 1939, **I**, 315), (*ii*) iodine as such by decomposing the salt with heat (Bahl, Singh and Bali, *J. Indian Chem. Soc.*, 1941, **18**, 587), (*iii*) available oxygen by the method adopted by Partington and Bahl (*J. Chem. Soc.*, 1934, 1086).

TABLE I

*Cobalt salt prepared by the action of disodium paraperiodate on cobalt sulphate*

| Sample | Cobalt | Iodine | $O_2$ (available). |
|---|---|---|---|
| 1. | 27·58% | 29·04% | 11·15% |
| 2. | 27·47 | 29·48 | 11·56 |
| 3 | 27·50 | 29·11 | 11·57 |

TABLE II

*Cobalt salt prepared by the action of potassium metaperiodate on cobalt nitrate*

| Cobalt | Iodine | $O_2$ (available) |
|---|---|---|
| 25·36% | 28·2% | 12·67% |
| 25·58 | 28·4 | 12·61 |
| 25·41 | 28·0 | 12·64 |

The values in Table I agree with the formula of cobalt iodate, $CoO_2$, $Co(IO_3)_2$, $10H_2O$, calculated values being Co, 27·21 ; $I_2$, 29·33 ; $O_2$(available), 11·01%.

The results in Table II correspond with the formula of cobalt dimesoperiodate, $Co_4I_2O_{11}$, $12H_2O$, the calculated values being Co, 25·78 ; $I_2$, 27·80 ; $O_2$(available), 12·36%.

### *The Periodates of Nickel*

Ramelsberg (*Pogg. Ann.*, 1868, **134**, 514) found that a green solution was obtained by the action of periodic acid on nickel carbonate, and a mixture of nickel dioxide, iodate and periodate were left undissolved. The green solution on crystallisation deposited pale green quadratic prisms of the composition, $7NiO, 4I_2O_7, 49\text{-}63\ H_2O$. Kimmins (*J. Chem. Soc.*, 1884, **55**, 148) obtained a greenish yellow amorphous precipitate of nickel mesoperiodate, $Ni_3(IO_5)_2$, by boiling sodium paraperiodate with a solution of nickel sulphate and a bluish green gelatinous precipitate of nickel dimesoperiodate, $Ni_2I_2O_9$, by treating a solution of potassium dimesoperiodate with nickel sulphate.

It has been found that a light green precipitate of the composition, $Ni_5(IO_6)_2, 13H_2O$, is formed by the action of disodium paraperiodate on nickel sulphate and a dirty green precipitate of the composition by the interaction of a hot solution of potassium metaperiodate and nickel chloride. The precipitate in both the cases was filtered, washed with water and dried at 45° in a hot air-oven. The salts were analysed in the same way as in case of cobalt salts given above.

TABLE III

*Nickel salt prepared by the action of disodium paraperiodate on nickel sulphate*

| Sample. | Nickel. | Iodine | $O_2$(available) |
|---|---|---|---|
| 1. | 31·01% | 27·85% | 12·13% |
| 2. | 30·89 | 27·67 | 12·27 |
| 3. | 31·17 | 28·03 | 12·25 |
| 4 | 31·23 | 27·74 | 12·06 |

TABLE IV

*Nickel salt prepared by the action of potassium metaperiodate on nickel chloride*

| Nickel. | Iodine | $O_2$(available). |
|---|---|---|
| 24·56% | 29·88% | 12·99% |
| 24·77 | 29·69 | 13·52 |
| 24·04 | 29·95 | 13·17 |

These results (Table III) agree with the formula of nickel paraperiodate with $Ni_5(IO_6)_2$, $13\ H_2O$, the calculated values being Ni, 31·67%; $I_2$, 27·50% ; $O_2$(available), 12·12%.

The results in Table IV correspond with the formula $NiO, 2I_2O_7, 25H_2O$, the calculated values being Ni, 24·41 ; $I_2$, 29·75 ; available oxygen, 13·13%.

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# GLUCOSE DEHYDROGENASE FROM GERMINATED SEEDS OF GREEN AND BLACK GRAMS (*PHASEOLUS RADIATUS* AND *PHASEOLUS MUNGO*, LINN.)

By K. P. Basu and J. N. Karkun

An oxidising enzyme from germinating green gram (and black gram) is described. It acts on glucose both aerobically and anaerobically and is, therefore, a perfect dehydrogenase. Methylene blue cannot be used as a hydrogen acceptor. It inhibits the enzyme by about 25% 2.6-Dichlorophenol-indophenol blue can act as an acceptor Galactose and mannose are also oxidised by the same enzyme and the latter is, therefore, group-specific. Fructose, xylose, arabinose are not affected. Narcotics inhibit the dehydrogenase, while potassium cyanide and hydrogen sulphide inhibit the oxidase factor. Flavin, adrenaline and ascorbic acid cannot act as carriers but glutathione can, the acceleration being about 8%. The enzyme appears to contain an aldehyde group, like Harrison's glucose dehydrogenase from animal sources The product of oxidation is probably gluconic acid. Physiological significance of the presence of the enzyme in plants is discussed

In course of some experiments, it was noticed that an aqueous extract of germinated seedlings of green gram (*Phaseolous radiatus*) absorbs a large amount of oxygen, when shaken in a Warburg-Barcroft vessel. The phenomenon occurred without the apparent addition of any substrate. Heating of the solution to 60° for 5 minutes prior to placing it in the vessel stopped the process completely showing that the phenomenon was due to the presence of some oxidising enzyme: The fact that the process was being continued without the apparent addition of any substrate, might be due to the donator being already present in the extract. With this point in view, attempts have been made to characterise the enzyme in question. With this purpose the solution is first dialysed in parchment paper against large volumes of distilled water and then different substances are added to the dialysed extract and the oxygen uptake is noted. It is found that addition of glucose to the dialysed extract produces a marked increase in the absorption of oxygen showing that the enzyme in question acts on glucose. Preliminary phenylhydrazine tests for glucose in the original extract have also been performed and characteristic crystals of osazone are found under the miscroscope, thus giving an indirect support to the previous conclusion.

Enzymes acting on glucose have been detected in widely different sources. Quastel and Wooldridge (*Biochem. J.*, 1928, **22**, 689) found this enzyme in *B. coli.* Muller (*Biochem. Z.*, 1929, **213**, 211) detected this enzyme in *Aspergillus niger.* He believed it to be an oxidase, in as much as it did not accelerate the reduction of methylene blue nor was hydrogen peroxide formed in the process of glucose oxidation. Harrison (*Biochem. J.*, 1931, **25**, 1016) was first to isolate glucose dehydrogenase from animal sources. The enzyme converted glucose into gluconic acid (*Biochem. J.*, 1932, **26**, 1295). It could function both anaerobically (with methylene blue as hydrogen acceptor) and aerobically in oxygen with *cytochrome-C* as a carrier (Hawthrone and Harrison, *Biochem. J.*, 1939, **33**, 1573). A co-enzyme was necessary for its activity as was first shown by Mann (*ibid.*, 1932, **26**, 785) and later confirmed by Harrison (*ibid.*, 1933, **27**, 383). Ogston and Green (*ibid.*, 1935, **29**, 1983) studied the action of different carriers on the enzyme and showed that methylene blue, yellow pigment and glutathione could accelerate the reaction. Harrison (*Proc. Roy. Soc.*, 1933, **B**, **113**, 150) also studied the chemical nature of the enzyme and showed that the enzyme contained an aldehyde group.

Franke and Lorenz (*Annalen*, 1937, **532**, 1) and Franke and Deffner (*ibid.*, 1939, **541**, 117) studied Muller's oxidase and showed that it was not an oxidase, but a dehydrogenase in as much as it could use quinone, indophenol derivatives and *p*-phenylenediamine as hydrogen acceptors. It also oxidised glucose to gluconic acid.

Ogura (*Acta Phytochim.*, 1939, **11**, 127) also detected a glucose dehydrogenase in *Aspergillus oryzae*. It differed from that of Muller and Franke in that it did not react directly with oxygen. Methylene blue could not serve as a hydrogen acceptor and in this respect it was identical with Muller's and Franke's enzyme but different from Harrison's. Mention should also be made of Yudkin's work (*Biochem. J.*, 1934, **28**, 1463) on the enzyme of *B. coli* and of Tarr's work (*ibid.*, 1933, **27**, 141) on the enzyme of the spores of vegetable tissues.

Thus, while there is so much study about the nature and action of the enzyme from animal and bacterial sources and from molds, no evidence has been presented, as yet, of its presence in higher plants. The discovery of the enzyme in germinating green gram is thus interesting, it being the first observation of its kind in higher plants and consequently a study of the properties and action of this enzyme has been made. It has been found that the enzyme is a dehydrogenase of "aerobic type", functioning both aerobically and anaerobically. Methylene blue cannot serve as a hydrogen acceptor in anaerobic oxidation but quinone and dichlorophenol derivatives can. Narcotics inhibit the enzyme very greatly while potassium cyanide and hydrogen sulphide inhibit the aerobic activity of the enzyme without affecting the dehydrogenating action. Like Harrison's enzyme, it can use glutathione as a carrier and seems to contain an aldehyde group. Unlike Harrison's enzyme its action is inhibited rather than accelerated by methylene blue and it requires no co-enzyme.

## EXPERIMENTAL

Most of the experiments were carried out under aerobic conditions. The anaerobic method was adopted only in the case where the chemical nature of the enzyme was determined.

Aerobic experiments were done in Warburg—Barcroft apparatus. One Barcroft vessel contained the enzyme, buffer and water without substrate to find out the amount of oxygen absorbed in the blank. Some amount of oxygen absorption in the blank was always found even after continuing the dialysis of the aqueous extract long enough and it was always taken into account. The inner cup of all vessels contained 0·3 ml. *N*-NaOH and filter paper, according to the technique of Dixon and Elliott (*Biochem. J.*, 1930, **24**, 820).

It must, however, be noted that the oxidising capacity of different enzyme preparations varied from preparation to preparation and as such no comparison between results with different preparations are possible. However, each series of experiments was carried out with one and the same enzyme solution and if possible, at the same time.

Anaerobic experiments were done in Thunberg tubes. In each experiment a series of tubes was used, each containing a total volume of 4·5 c.c. of the contents. Each tube contained 0·5 c.c. of 1/5000 dichlorophenol-indophenol blue, 0·5 c.c. of *M*/10 glucose solution and 1 c.c. of enzyme solution. The tubes were evacuated at room temperature with the help of a Cenco Hyvac pump. The time for complete reduction was observed. Blank experiments were also performed side by side Both aerobic and anaerobic activity was measured at 38°.

*Preparation of the Enzyme.*—Seeds of green gram were washed and then kept immersed in water for 24 hours, during which they swelled and the outer coats burst, the radicle of each seed appearing to come out of the micropyle. The water was then drained away and the seeds were spread on moist sand in a shady place for germination. When the plumule just began to come out—a process which needed about 3 days—the seeds were washed free from sand, finally washed with distilled water and ground well in a mortar with acid-washed sand.

About twice its volume of distilled water was then added and the whole allowed to stand about half an hour in a refrigerator, after which the extract was pressed out of muslin. The extract was taken in a conical flask and allowed to stand for another 45 minutes to 1 hour in the refrigerator, during which time a large amount of starch and proteins of the globulin type separated at the bottom. The clear extract from the top was syphoned out and dialysed in a parchment paper against large volumes of distilled water with frequent changes. For aerobic experiments, extracts usually dialysed for 3 days were found to be most convenient, whereas for anaerobic activity measurements, 2 days' dialysis sufficed.

Proceeding in exactly the same way a similar enzymic preparation was obtained from black gram (*phaseolus mungo*, Linn.). Since in every case except the optimum $p_H$, the properties of the latter enzyme are very much akin to those of the enzyme in green gram, it was not studied in detail. Only the optimum $p_H$ was determined in this case. The results are given below.

TABLE I

*Determination of optimum $p_H$*

| | Green gram | | | | | | Black gram | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $p_H$ of the medium | 5·9 | 6·2 | 6·5 | 6·8 | 7·1 | 7·4 | 5·6 | 5·9 | 6·2 | 6·5 | 7·1 | 7·4 |
| Oxygen absorption in /ul per 30 minutes | 70·6 | 126·7 | 193·8 | 120·7 | 76·0 | 54·8 | 132·0 | 183·0 | 125·8 | 69·4 | 65·6 | 69·0 |

In each of the Barcroft vessels were taken 2 c.c. of the enzyme solution, 1 c.c. of *M*/10 glucose and 4 c.c. of *M*/6 phosphate buffer and water making a total volume of 8 c.c. The final concentration of the buffer was nearly *M*/10.

A difficulty met with in the determination of optimum $p_H$ was that the acidic oxidation product of the enzyme changed the $p_H$ of the medium considerably towards the acid side. It was avoided by the use of phosphate buffer at a higher concentration. Preliminary trials showed that *M*/6 phosphate buffer added in 4 c.c. portions to every 7-8 c.c. of the total volume would maintain the $p_H$ constant for at least 3 hours. Further, at this concentration it was not inhibitory to the enzyme system. Table II shows the effect of concentration of the substrate on the enzymic activity.

TABLE II

Contents of the cup : 2 c.c. enzyme, 1 c.c. substrate, 4 c.c. phosphate buffer and 1 c.c. water. $p_H$ 6·5. Temperature = 38°

| Molarity of the substrate | M/40 | M/60 | M/80 | M/100 | M/200 | M/400 |
|---|---|---|---|---|---|---|
| Oxygen absorption in /ul per two hours | 950·4 | 944·2 | 824·1 | 654·1 | 446·7 | 359·7 |

The maximum rate reached when the concentration of the substrate was about 0·025 *M*. The half-speed concentration (*i.e.* the Michaelis constant $K_m$) is very nearly equal to 0·005 *M*, a value which like that of Harrison's enzyme (0·007 *M*) is an exceptionally high value for an oxidising enzyme.

*Inactivation by Heat.*—The enzyme solution (5 c.c.) was placed in each of several test-tubes kept immersed for 10 minutes in baths at different temperatures ranging from 35° to 52°. The solutions were cooled and the activity of each sample measured manometrically by taking 2 c.c. portions of the enzyme solutions in every 4 c.c. portion of *M*/6 phosphate buffer and adding 1 c.c. of *M*/10 glucose to each of them. Up to 40° the activity remained intact, after which there was gradual inactivation and at 52° the enzyme was completely inactivated. The results are shown in Table III.

TABLE III

Temperature of the experiment = 38°

| Temperature of incubation | 35° | 40° | 42° | 44° | 48° | 50° | 52° |
|---|---|---|---|---|---|---|---|
| Oxygen absorption in /ul per hour | 267·7 | 270·3 | 268·7 | 203·2 | 87·4 | 17·1 | Nil |

*Temperature Coefficient.*—It is known that within the temperature zone, where there is practically no temperature inactivation of the enzyme system, the ratio of velocities at two temperatures, differing by 10° from one another, is a characteristic constant varying slightly with different enzyme systems and is near about 2 to 3. Experiments of this kind, performed with the enzyme in question, revealed a value near about 2·5 to 2·6. The following are the results (Table IV).

TABLE IV

| Temp. at which the activity is measured. | Activity (in /ul oxygen per hr.) | $Q_{10}$. |
|---|---|---|
| 25° | 56·2 | 2·59 |
| 35° | 145·8 | |
| 30° | 92·0 | 2·51 |
| 40° | 230·2 | |

TABLE V

| Enzyme | Substrate. | Temp. | $Q_{10}$. |
|---|---|---|---|
| Xanthine oxidase | Hypoxanthine | | 2·0 [1] |
| Root peroxidase | Leucomalachite green. | 5-15° | 2·0 [2] |
| | | 15-25° | 2·0 |
| *B. Coli* succinoxidase | Succinate. | 30-40 | 2·1 [3] |
| | | 40-50° | 2·1 |
| Glucose dehydrogenase of green gram | Glucose | 25-35° | 2·6 [4] |
| | | 30-40° | 2·5 |

It will perhaps be interesting to compare these values with those found with some other respiratory enzymes, as shown in the Table V.

### *Inhibitors*

*Action of Narcotics.*—According to the classical work of Keilin (*Proc. Roy. Soc.*, 1928-29, **B**, **104**, 251) the inhibitory action of narcotics on the activity of respiratory enzymes is due to their action on the dehydrogenating part of the latter. The narcotics become absorbed on the enzyme surface and the reaction velocity is inhibited owing to the displacement of the reacting substance in question by them. If, therefore, the enzyme is left for sometime in contact with the narcotic before the addition of the substrate, the maximum inhibitory power is exerted. The following experiments were done to see the action of narcotics on the enzyme.

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[1] Dixon and Thurlow (*Biochem. J.*, 1924, **18**, 976).

[2] Willstätter and Weber (*Annalen*, 1926, **449**, 175).

[3] Quastel and Whetham (*Biochem. J.*, 1924, **18**, 519).

[4] Present investigation.

2 C.c. portions of the enzyme were taken in different Barcroft vessels with 3 c.c. portions of phosphate buffer ($M/6$) 1 C.c. of narcotic at suitable concentration was added to each and the cups were shaken for 20 minutes in the thermostat with the taps closed. At the end of this interval, 1 c.c. of substrate was added to each and the oxygen uptake was measured. The activity was compared with that of the control which was also treated in the same manner excepting exposure to the narcotic and the inhibition noted. The results are tabulated below.

TABLE VI

Temperature of the experiment = 38°. Duration of the experiment = 1 hr. 20 mins.

| Inhibitor. | Final conc | % inhibition. | Inhibitor. | Final conc | % inhibition. |
|---|---|---|---|---|---|
| Vanillin | 5% | 95 | Barbitone | 5% | 69 |
| | 1 | 63 | | 1 | 39 |
| | 0·1 | 18 | | 0·1 | 26 |
| Urethane | 5 | 88 | Octyl alcohol | 0·1 | 99 |
| | 1 | 52 | | 0·02 | 82 |
| | 0·1 | 12 | | | |

Unfortunately the enzyme solutions employed in the experiments with different inhibitors were of different degrees of purity, and as such the results are not strictly comparable. One thing is, however, noticeable; octyl alcohol is highly inhibitory to the enzyme and with its suitable concentration the activity can be practically completely supressed. The action of vanillin is also noticeable.

*Action of Potassium Cyanide*.—Cyanide at a concentration of 0·001$M$ inhibits the enzyme by about 66%. On increasing the concentration, the inhibition also increases and a concentration of 0·01 $M$-potassium cyanide inhibits the enzyme activity by about 91%. In carrying out these experiments, alkali in the inner cup of the Barcroft vessel was replaced by an alkali-cyanide mixture of suitable concentration according to the direction of Krebs (*Biochem. J.*, 1935, **29**, 1620). The results are summed up in Table VII.

TABLE VII

*Potassium cyanide*

$M/6$-phosphate buffer = 4 c.c. Enzyme soln. = 2 c.c. Glucose = 1 c.c. KCN or water (control expt.). Temp. = 38°.

| Time in min. | 0 | 15 | 30 | 45 | 60 | 75 | 90 |
|---|---|---|---|---|---|---|---|
| Substances | Oxygen absorption in /ul | | | | | | |
| Glucose alone | 0 | 20·1 | 39·2 | 60·2 | 91·4 | 123·5 | 174·7 |
| Glucose and KCN (0·01 $M$) | 0 | 4·1 | 6·3 | 11·5 | 12·0 | 13·8 | 15·0 |
| Glucose and KCN (0·001 $M$) | 0 | 15·2 | 30·7 | 41·7 | 47·6 | 51·2 | 59·5 |

TABLE VIII

*Other inhibitors*

1 C.c. inhibitor or water (control expt.). Duration of the expt. = 1 hour 30 min. Other conditions same as in Table VII.

| Inhibitors. | $O_2$ absorption in /ul<br>In presence of inhibitor | Control | Inhibition. |
|---|---|---|---|
| Sodium pyrophosphate ($M/50$) | 195·5 | 212·5 | 8·0% |
| $M/250$-$Na_2S$ | 70·8 | ,, | 66·7 |
| $M/10$-NaF | 175·3 | ,, | 17·5 |
| $CuSO_4$ (0·2 mg) | 95·6 | ,, | 55·0 |
| Fe (0·2 mg) | 213·2 | ,, | Nil |

*Other Inhibitors.*—Sodium sulphide ( $M/250$ ) produces a strong inhibition on the oxidase factor of the enzyme. Inhibition by NaF ($M/10$) and sodium pyrophosphate ($M/50$) is relatively small. The addition of 0·2 mg. of copper inhibited the enzyme by 55% while iron at similar concentrations both in the reduced and oxidised forms was without any effect (Table VIII).

## *Specificity*

*Specificity of the Donator.*—The dehydrogenase of the green gram oxidises galactose and mannose in addition to glucose. Fructose is not very much oxidised, while xylose and arabinose are not oxidised at all. The action on galactose and mannose is appreciable in comparison with that on glucose, as the following table will show.

TABLE IX

| Substrate | Glucose | Galactose | Mannose |
|---|---|---|---|
| Oxygen absorption in /ul per 2 hrs | 642·3 | 403·7 | 213·7 |

The glucose dehydrogenase of Harrison (*Biochem. J.*, 1931, **25**, 1016) also has appreciable action on galactose and mannose. Franke and Deffner (*loc. cit.*) in working with Muller's oxidase have also stated that the rates of oxidation of glucose, mannose and galactose by the enzyme are in the ratio 1 . 0·07 : 0·14. The enzyme from *Aspergillus oryzae*, isolated by Ogura, similarly acts on mannose, galactose and xylose. Whether all these substances are oxidised by the same enzyme or by different enzymes in the same preparation, is not definitely known and no experiments in this line have been carried out. It seemed, therefore, of interest to study this phenomenon since it might yield information as to whether the enzyme is specific for glucose, or it is group-specific. With this object in view the following experiments were done.

If two substrates are oxidised by the same enzyme, it is to be expected that the rate of oxidation of the two substrates together in optimum concentration, will be less than the sum of the oxidation rates of each substrate alone. When glucose was added to the enzyme in optimum concentration, the further addition of galactose or mannose was not found to increase the rate of oxidation. Table X shows the results

TABLE X

Competition between glucose and galactose.

| | | | | |
|---|---|---|---|---|
| Glucose | 0·025 $M$ | 0·025 $M$ | 0 | 0 |
| Galactose | 0 | 0·025 $M$ | 0·025 $M$ | 0·05 $M$ |
| $O_2$ uptake (ul/30 mins.) | 125·0 | 112·0 | 79·7 | 75·2 |

Competition between glucose and mannose

| | | | | |
|---|---|---|---|---|
| Glucose | 0·025 $M$ | 0·025 $M$ | 0 | 0 |
| Mannose | 0 | 0·025 $M$ | 0·025 $M$ | 0·025 $M$ |
| $O_2$ uptake (ul/30 mins.) | 106·2 | 89·0 | 37·4 | 37·0 |

Preliminary trials showed that optimum concentrations of galactose and mannose were reached at 0·02 $M$ and 0·017 $M$ respectively. The above experiments thus clearly show that the same enzyme acts on glucose, galactose and mannose. The enzyme is, therefore, group-specific.

*Specificity of the Acceptor.*—As mentioned before, the enzyme catalyses the oxidation of glucose by molecular oxygen and by oxidation-reduction indicators such as 2 : 6-dichlorophenol-indophenol derivatives. Methylene blue is unable to act as an hydrogen acceptor. It inhibits the enzyme action by about 25%. Appropriate experiments also showed that flavin, adrenaline and ascorbic acid were incapable of acting as intermediate carriers while glutathione could, the acceleration being about 8%.

TABLE XI

*Effect of carriers on glucose dehydrogenase*

| Carrier. Name | Conc. | /ul $O_2$ per hr. absorption with control. | carrier. | %accleration. |
|---|---|---|---|---|
| Flavin | 10γ/c.c. | 256·8 | 248·9 | Nil |
| Adrenaline | (1 mg/8 c.c.) | 225·5 | 230 4 | ,, |
| | | (with adrenaline alone = 10) | | |
| Glutathione | (4 mg /8 c c.) | 238·1 | 257·7 | 8 2 |
| Ascorbic acid | (5 mg /8 c.c.) | 250·0 | 296·3 | Nil |
| | | (with ascorbic acid alone = 200·2) | | |
| Methylene blue | (1/60,000) | 211·1 | 157 9 | 25 2 (inhibition) |

TABLE XII

*Effect of xanthine oxidase on glucose dehydrogenase*

Temp. of the expt. = 38°. Dye used = 0·5 c.c. of (1/5000)2 : 6-dichlorophenol-indophenol

| No. of tube. | Glucose dehydrogenase of green gram. | Glucose (M/10). | Xanthine oxidase. | Reduction time. |
|---|---|---|---|---|
| 1 | 1 c c. | 0 5 c. c. | 1 c c | >3 hours |
| 2 | 1 | 0·5 c.c. | ,, | 18 mins |
| 3 | 1 | — | 1 c.c | >3 hours |
| 4 | 1 | — | — | 3 hours |

### *Purification of the Enzyme*

Precipitation with dilute acetic acid, acetone, alcohol and alcohol-ether mixtures was tried but all yielded inactive preparations. Precipitation by half or full saturation with ammonium sulphate in acid, alkaline and neutral regions was tried but with no success. The enzyme seemed to be adsorbed partly on kaolin but no satisfactory method of elution was found out. It should also be noted in this connection that seedlings (3 days old) yielded the most active preparation and after 5 days the activity was very low.

*Absence of Co-enzyme.*—The enzyme was not inactivated by dialysis. Further, the addition of boiled extract did not increase the activity. No co-enzyme is, therefore, necessary for this dehydrogenase.

*Aldehyde group of the Enzyme.*—Working with the glucose dehydrogenase of animal source Harrison (*Proc. Roy. Soc.*, 1933, **B.**, **113**, 150) found it to contain an aldehyde group. The principle of his experiment was to see the action of xanthine oxidase and of sodium bisulphite on the enzyme. It is known that xanthine oxidase acts on aldehydes (as also on purines) and that sodium bisulphite in acid *p*H combines with aldehydes. If, therefore, the enzyme in question contained an aldehyde group, it should be inhibited by xanthine oxidase as well as by sodium bisulphite in acid *p*H. Experiments corroborated this fact. In order to show that the inhibition by xanthine oxidase was not due to mutual inactivation of the two enzymes, Harrison showed that his dehydrogenase did not inhibit the activity of xanthine oxidase at all. Further in a second series of experiments he showed that heating of the xanthine oxidase to progressively increasing temperatures, previous to incubation with glucose dehydrogenase, decreased its property of inhibiting the latter, thus showing definitely that the inhibition of glucose dehydrogenase was due to the activity of the xanthine oxidase.

As xanthine oxidase might act on the aldehyde or purine group, he confirmed his assumption by allowing sodium bisulphite in acid *p*H to act on his enzyme and found definite inhibition with the latter, thus establishing beyond doubt the presence of an aldehyde group in the enzyme.

Working in exactly the same way with the dehydrogenase of the green gram, it was found that xanthine oxidase definitely inhibited the enzyme Xanthine oxidase was prepared according to the method of Dixon and Kodama (*Biochem. J.*, 1926, **20**, 1104). The enzyme solution was prepared by dissolving a suitable amount of the powder in water, bringing to the required $p_H$ (6·5) by cautious addition of dilute sodium hydroxide and centrifuging to obtain a perfectly clear solution. 1 C.c. of the enzyme solution could decolourise 0·5 c.c. of 1/5000-methylene blue in 5 minutes with 0·2 mg. of hypoxanthine as the substrate. The results are given in Tables XII and XIII. Because of the inability of the dehydrogenase of green gram to decolourise methylene blue, 2 : 6-dichlorophenol-indophenol blue was used in measuring its activity. The activity of xanthine oxidase was measured, as usual, with methylene blue as hydrogen acceptor.

The fact that in tube (4) the time of decolourisation of indophenol blue is less than that of (1) and (3) might be due to the fact that a small amount of glucose remained tenaciously in the extract and was not removed even after prolonged dialysis.

TABLE XIII

*Effect of heated xanthine oxidase on glucose dehydrogenase of green gram*

Temp. = 38°. Time of heating = 5 minutes

| No. of tube. | Dehydro-genase. | Glucose M/10. | Xanthine oxidase. | Reduction time of | | No of tube. | Dehydro-genase | Glucose M/10 | Xanthine oxidase. | Reduction time of | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | indo-phenol. | methylene blue | | | | | indo-phenol. | methylene blue. |
| 1 | 1 c c | 0 5 c c. | — | 16 mins. | — | 4 | 1 c.c. | 0·5 c c. | 1 c.c. (heated to 65°) | >3 hrs. | $9\frac{3}{4}$ mins. |
| 2 | ,, | ,, | 1 c.c. (unheated) | >3 hrs. | 5 mins. | 5 | ,, | ,, | 1 c c (heated to 70°) | 25 mins. | 31 mins. |
| 3 | ,, | ,, | 1 c.c. (heated to 55°) | >3 hrs. | $7\frac{1}{2}$ mins | 6 | ,, | ,, | 1 c c. (heated to 75°) | $16\frac{1}{3}$ mins. | — |

From the results in Tables XII and XIII it is seen that xanthine oxidase appears to inhibit the activity of glucose dehydrogenase of the green gram. That the diminution of the activity of the latter is not due to the mutual action of the two enzymes was shown. Thus it was found that 1 c.c. of the above xanthine oxidase solution used, decolourised 0·5 c.c. of 1/5000 methylene blue in nearly 5 minutes in presence of 0·2 mg. of hypoxanthine and 1 c.c. of the glucose dehydrogenase in question. The latter enzyme, therefore, did not inhibit the former.

For confirmation of the presence of the aldehyde group in the enzyme the action of sodium bisulphite, as mentioned above, must be seen. But several difficulties arose. Thus when sodium bisulphite (in acid $p_H$) was added to a mixture containing glucose dehydrogenase of the green gram and 2 : 6-dichlorophenol-indophenol blue, the colour of the latter disappeared instantly, making anaerobic experiments impracticable. In aerobic experiments also there was a large oxygen uptake due to autoxidation of the bisulphite. Preliminary incubation of sodium bisulphite produced no result as was previously shown by Harrison (*loc. cit.*). However, it was found that some sort of competition took place between sodium bisulphite (in acid $p_H$ only) and glucose for the enzyme surface in all aerobic experiments. This could not be the case if sodium bisulphite did not tend to combine with the aldehyde group of the enzyme.

### *Products of Oxidation*

It was mentioned before that the product of oxidation of glucose is acidic, as was evinced by the change in the $p_H$ of the solution when buffer of low concentration was used in the experiments. Harrison (*loc. cit.*) working with glucose dehydrogenase of animal tissues isolated gluconic acid as the oxidation product. The same substance was also found by Franke and Lorenz (*loc. cit.*) and by Ogura (*loc. cit.*) as the oxidation product of glucose by their respective enzymes. Attempts were, therefore, made to see whether the oxidation product of glucose by the action of the enzyme from green gram was identical with gluconic acid. No satisfactory quantitative method has as yet been developed. However, proceeding in a method similar to that of Harrison (*loc. cit*) with slight modifications, some crystals of calcium gluconate were found in alcoholic medium. In broad outline the method involves precipitation of the protein with 80% alcohol, adding basic lead acetate to the concentrated filtrate to precipitate gluconic acid as lead salts, removing the lead by hydrogen sulphide. and addition of calcium carbonate to the acidified liquid. The calcium gluconate is then precipitated with alcohol and crystallised from 30% alcohol.

## DISCUSSION

From the above results, it seems that the enzyme of green gram stands midway in properties between the dehydrogenase of Harrison and that of Muller, Franke and Ogura. Like Harrison's enzyme it is a perfect dehydrogenase, functioning both aerobically and anaerobically, using glutathione as a hydrogen acceptor and having the same aldehyde group in the enzyme molecule. The similarity is pushed still further by their high Michaelis constant. Unlike Harrison's enzyme it cannot use methylene blue as a hydrogen acceptor but can decolourise 2:6-dichlorophenol-indophenol blue with advantage. It does not require the presence of a co-enzyme and in these respects it is similar to the enzyme systems of the molds. Some properties are, however, common to all of them; thus all of them oxidise glucose to gluconic acid, can function both aerobically (except the enzyme of *aspergillus oryzae* of Ogura) and anaerobically. All are group-specific rather than strictly specific to glucose alone. The inability of all of them except Harrison's enzyme to decolourise methylene blue, points out that the oxidation-reduction potential of the latter enzyme is more negative than that of the former. Is it then due to the fact that all of them contain the same aldehyde group (active group ?) but a different colloidal carrier or träger ?

The sensitivity of the oxidase factor to the action of potassium cyanide and hydrogen sulphide (and to a less extent to fluoride and pyrophosphate) points to the probability of cytochrome systems functioning in the aerobic process But the fact that even at a concentration of 0·01$M$ potassium cyanide the inhibition is not 100% also points to the presence of some additional cyanide-stable system or systems. Several carriers were tested and all were found to be inactive with the exception of glutathione but other carriers, such as pyocyanine were not available and as such the problem cannot be said to be finally settled.

It has been shown by Hawthron and Harrison (*loc. cit.*) that in the aerobic oxidation of glucose glucose dehydrogenase from animal tissues can use cytochrome *a*, *b* or *c* as carriers, provided some other factor, diaphorase of Euler, is present. In the case of the enzyme from green gram, it is not known whether any one of *a*, *b* and *c* or all of them can function as carriers or whether the presence of diaphorase is necessary for reduction of cytochrome systems. And indeed it cannot be known unless some method of purifying the enzyme in question is found and herein we failed inspite of a good number of careful experiments with different reagents.

### *Physiological Significance*

The isolation of glucose dehydrogenase in green and black grams raises a number of questions as regards its possible significance to them and to the plant systems at large. Are these plants dependent for their supply of energy upon the oxidation of glucose in their life-course or since the enzyme is found in germinated seeds, at least in the period of germination ? In view of the fact that in aqueous extract of the enzyme there is always found some amount of glucose even inspite of prolonged dialysis with consequent oxygen uptake in the blank, the conclusion seems unavoidable. However, considering the wide diversity which plants display amongst themselves, such generalisation now is premature until a systematic and careful study is made of the distribution and mode of action of the enzyme in different plant systems or at least in some representative members.

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# CHEMICAL EXAMINATION OF THE SEEDS OF *VATERIA INDICA*. PART I. COMPONENT FATTY ACIDS OF THE FAT

By C. Venkatarao and M. Narasingarao

The fat from the seeds of *Vateria indica* contains 92·6% insoluble mixed fatty acids composed of 60 7% solid acids and 39·3% liquid acids. The composition of the fatty acids is found to be 0 2% lower acid, 0·7% myristic acid, 13% palmitic acid, 45·1% stearic acid, 0·4% arachidic acid, 42·5% oleic acid and 0 1% linoleic acid The non-saponifiable matter is mainly composed of sitosterol and a trace of another sterol whose bromoacetate melts at 120-23° to a dark coloured liquid Further, the fat on steam-distillation yields 0 05% of a terpenoid oil having an iodine value of 148.

The fat known as Malabar-tallow is obtained from the seeds of *Vateria indica* (N. O. Deptero-carpaceæ, Vernacular, *Safed Damar*), a large ever-green tree found in Mysore, South Canara, Malabar and Travancare. The seeds yield on boiling with water 20% of a solid greenish-white fat with a pleasant flavour and agreeable taste, which is mainly used for edible purposes in South Kanara. This fat was used to be exported to Europe some years ago from Mangalore for uses as chocolate fat. Menon ("Manufacture of Soap in India") reports that this fat can replace tallow in the preparation of household and good toilet soaps. Further it has been shown to be suitable for yarn sizing and compares well with the high-class hydrogenated fats and animal tallows. A sample of the fat was obtained through the courtesy of the Forest Utilization Officer, Madras.

The present work is undertaken to investigate thoroughly the fatty acid composition of the fat since conflicting statements are made by the previous authors regarding the identifications of the various acids present (Lewkowitsch, "Chemical Technology of Oils and Fats", Vol. II, p. 590 ; Forest Research Reports in India, 1930-31, p. 224 ; 1931-32, p. 72 ; Jones, Hilditch and Saletore, *J. Soc. Chem. Ind.*, 1931, 468T ; Puntambekar and Krishna, *J. Indian Chem. Soc.*, 1933, **10**, 205), and also to find out the glyceride structure of the fat. Chemical and physical constants of the fat are given in Table I along with those observed by others.

TABLE I

| | Present workers. | Forest Reserch Reports, India. | Jones & co-workers | Puntambekar & Krishna |
|---|---|---|---|---|
| M p. | 36-37° | — | — | 40° |
| $d^{10\ 3}_{33\ 5}$ | 0 8989 | — | — | at 25°, 0·9120 |
| Ref index* | 1·4578 at 40° | 1·4556 at 25° | — | at 25°, 1·4556 |
| Sap. value | 191·1 | 175 | 184·8 | 190·4 |
| I. value | 36·72 (Wij's) | 40 15 | 42·8 | 40 0 (Hanus) |
| Non. sap. | 0 588% | — | — | 0·8% |
| Hehner value | 92·6 | — | — | 97 6 |
| Acid value | 2 88 | 1 4 | 8 8 | 1 4 |

* With Butyro-refractometer

705 G of the fat were saponified with strong alcoholic solution of sodium hydroxide and the fatty acids were separated by splitting the soap. The chemical and physical properties of these insoluble acids and those of the liquid and solid acids separated by the lead salt-alcohol method (Twitchell, *Ind. Eng. Chem.*, 1921, **13**, 806) with slight modifications are given below along with the recordings of others.

TABLE II

| Mixed acids | Present workers | Forest Research Reports | Jones & co-workers | Puntambekar & Krishna. |
|---|---|---|---|---|
| Sap equiv. | 289 4 | 286 | — | 286 |
| I. value | 38 8 | 38 6 | — | 38 6 |
| Sol Pt | 55 9° | — | — | — |
| M. p. | 55·6° | — | — | — |
| Sol. acids(%) | 60 7 < S.P. 280·7<br>I.V. 7 07 | 53 | 55·6 | 61 |
| Liq. acids(%) | 39·3 < S E. 280·0<br>I.V. 87·9 | 47 | 44 4 | 39 |

Ether soluble portion of the lead salts are mixed up with the alcohol solubles.

The fatty acids were converted into methyl esters and the esters were subjected to fractional distillation under reduced pressure of 2 mm.

TABLE III

*Fractionation of esters of liquid acids*

Esters, 132·5 g., S.E., 293·6; I V., 83·8.

| Fr. No. | Temp of fraction. | Wt of fraction. | S E. | I.V. | Identifications |
|---|---|---|---|---|---|
| 1 | 82-139° | 3·5 g. | 259 6 | 53·2 | Lower acid ($C_{10}$), myristic, palmitic & oleic |
| 2 | 140-149° | 6·5 | 284·6 | 68 1 | Myristic, palmitic and oleic. |
| 3 | 149-151° | 16·2 | 294·0 | 80·0 | Palmitic & oleic. |
| 4 | 151-158° | 26·0 | 294·8 | 82·8 | Palmitic & oleic |
| 5 | 158° | 7 4 | 295·2 | 83 8 | Palmitic, oleic & linoleic. |
| 6 | 159-175° | 13·4 | 295·5 | 84·5 | Palmitic, oleic & linoleic. |
| 7 | 175° | 29·5 | 295·8 | 85·9 | Oleic & linoleic |
| 8 | Residue | 30·0 | 295·7* | 85·4 | Oleic, linoleic & non-sap |

* Corrected value.

TABLE IV

*Fractionation of esters of solid acids*

Esters, 144·9 g.; S.E, 294·6; I V. 6 91.

| Fr. No. | Temp of fraction. | Wt. of fraction. | S E. | I V. | Identifications. |
|---|---|---|---|---|---|
| 1 | 120-141° | 2 8 g | 265 6 | 9 8 | Myristic, palmitic & oleic. |
| 2 | 142-149° | 5·2 | 285 8 | 6 1 | Palmitic, stearic and oleic. |
| 3 | 149-152° | 45 9 | 289.4 | 5 6 | ,, |
| 4 | 152-154° | 21 2 | 289 5 | 5 8 | ,, |
| 5 | 154-163° | 37·4 | 293 6 | 6·2 | ,, |
| 6 | 163-170° | 7·5 | 296·3 | 6·2 | ,, |
| 7 | 170-172° | 7·4 | 296·4 | 6·6 | ,, |
| 8 | Residue | 17 5 | 298·7 | 12 6 | Oleic, stearic & arachidic. |

Fraction No. 1 of the liquid esters gave a terpenoid oil, I.V. about 148. All the above identifications were carried out by usual methods of crystallisations and analysis for the chemical characteristics and finding the mixed melting points with authentic samples. Oleic acid was identified by oxidation with alkaline permanganate according to Lapworth and Mottram (*J. Chem. Soc.*, 1925, 1628) when dihydroxystearic acid, m.p. 130°, without any other secondary product, was obtained Further, the position of ethylinic linkage was determined by disruptive oxidation of the methyl oleate with potassium permangante in acetone medium (Armstrong and Hilditch., *J. Soc. Chem. Ind.*, 1925, **44**, 447) when azaelic and nonoic acids were obtained showing that the acid is $\Delta^{9\cdot 10}$-oleic acid. *iso*Oleic acid was found to be absent

Linoleic acid was identified by separating oleic and linoleic acids partially by lithium salt formation and crystalliation from alcohol and then oxidising with alkaline permanganate in cold, when pure tetrahydroxystearic acid, m.p. 171°, was obtained. Oleic acid and linoleic acids were further identified by bromination by the method of Eibner and Muganthaller and then separating the tetrabromide, m.p 114°, from petroleum ether almost quantitatively.

From the above identifications the acids are calculated on percentage basis and given below along with the recorded results of previous workers.

TABLE V

| | Present workers. | | | Forest Research reports. | Jones & co-workers. | Puntambekar & Krishna. |
|---|---|---|---|---|---|---|
| | Sol acid % (60·7 %) | Liq acid % (39·3%) | Total fatty acid (%) | | | |
| Lower acids ($C_{10}$) | — | 0·4 | 0·2 | — | — | — |
| Myristic | 0·3 | 1·4 | 0·7 | — | — | Inferred (not isolated) |
| Palmitic | 20·0 | 2·1 | 13·0 | 6 | 10·2 | — |
| Stearic | 71·1 | — | 43·1 | 45 | 38·9 | 59 |
| Arachidic | 0·7 | — | 0·4 | 2 | 3·1 | Lignoceric. |
| Oleic | 7·9 | 95·2 | 42·5 | 47 | 47·8 | 39<br>(Oleic & *iso*oleic) |
| Linoleic | — | 0·2 | 0·1 | — | — | — |

*Non-saponifiable Matter.*—The non-saponifiable matter obtained from the last fraction of the liquid esters was crystallised from methyl alcohol and acetone mixture (3:1) when balls of crystals in the form of plates separated which melted at 129-30° and gave all the colour reactions of sterols. The acetate gave crystals similar to the sterol itself melting at 127-29° on bromination of the acetates by the method of Windaus and Hauth (*Ber.*, 1906, **39**, 4378) no precipitate came down showing the absence of stigma and brassica sterols. However, on concentrating the ether solution, a crystalline substance separated. This on crystallisation from chloroform-alcohol mixture (1:1) melted at 120-22° into a dark coloured liquid.

*Steam-distillation of the Fat.*—100 G. of the raw fat were steam-distilled and 5 litres of distillate were collected and extracted with ether. The ether extract was washed with dilute alkali to remove the free fatty acid that came with the distillate and on evaporation yielded a small quantity (0·05 g.) of essential oil having I.V. 148. This resembled the terpenoid oil obtained from the first fraction of the liquid esters.

## CONCLUSION

The fatty acids of *Valeria indica* consist of myristic (0·7%), palmitic (13%), stearic (43·1%), oleic (42·5 ), arachidic (0·4%) and linoleic (0·1%) acids.

Puntambekar and Krishna (*loc. cit.*), mentioned the presence of *iso*oleic acid but they did not carry either oxidation methods or reconversion methods for confirmation. Repeated efforts by the present authors did not give any positive indication of its presence. From the last fraction of solid esters pure arachidic acid was isolated and identified. But no lignoceric acid could be detected.

Failure of Jones to detect the presence of myristic and linoleic acids may be attributed to the small quantity of fat at her disposal for carrying out the work and the small percentage of acids in the fat.

Presence of a new sterol whose bromo-acetate melted to a dark coloured liquid at 120-22° was indicated. Fine smelling essential oil (0·05%) on fat having iodine value of about 148 was isolated. Further work on the characterisation of the above is in progress.

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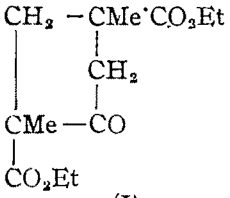
# ACTION OF SODIUM ON ETHYL β-METHYLBUTANE-αβδ-TRICARBOXYLATE. PART III. A SYNTHESIS OF *cis*-ALLOSANTENIC ACID

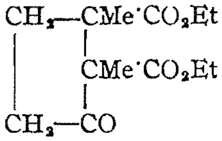
By Ram Narayan Chakravarti

In a previous paper it has been shown that the product of sodium condensation of ethyl β-methylbutane-αβδ-tricarboxylate on methylation followed by hydrolysis of the resulting product furnishes β-methylpentane-αβδ-tricarboxylic acid. The isomeric acid, γ-methylpentane-αγδ-tricarboxylic acid, m.p. 178°, has now been synthesised in a state of purity following the general method outlined in Part II The triethyl ester of the latter has been cyclised, hydrolysed and esterified to give ethyl 2 . 3-dimethyl*cyclo*pentan-1-one-3-carboxylate. This readily reacts with hydrogen cyanide and the cyanohydrin on dehydration, hydrolysis and reduction yields *cis*-allosantenic acid, m.p. 151-52°. The stereochemical configurations of the isomeric santenic acids cannot be regarded as definitely established.

In Part I (*J. Indian Chem. Soc.*, 1943, **20**, 173) it has been shown that the product obtained by the action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate on treatment with methyl iodide furnished chiefly ethyl 3 : 5-dimethyl*cyclo*pentan-1-one-3 : 5-dicarboxylate (I), since on hydrolysis the latter yielded β-methylpentane-αβδ-tricarboxylic acid (III, $R_1$=Me; $R_2$=H), m.p. 178-79°. The present paper deals with the synthesis and reactions of the isomeric γ-methylpentane-αγδ-tricarboxylic acid (III, $R_1$=H; $R_2$=Me) which might have been formed if the condensation product had the alternative structure (II).



(I)



(II)

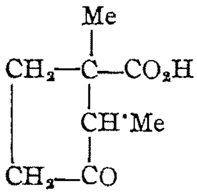
$CO_2H{\cdot}CHR_1{\cdot}CH_2{\cdot}CMe(CO_2H){\cdot}CHR_2{\cdot}CO_2H$

(III)

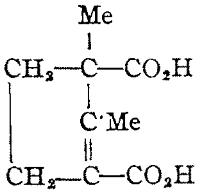
Ethyl αβ-dicyano-β-methylbutane-αδ-dicarboxylate (IV, R=H) (Banerjee, *J. Indian Chem. Soc.*, 1940, **17**, 425) on treatment with sodium ethoxide and methyl iodide under the conditions described in the experimental part affords ethyl γδ-dicyano-γ-methylpentane-αδ-dicarboxylate (IV, R=Me). This on hydrolysis furnishes γ-methylpentane-αγδ-tricarboxylic acid (III, $R_1$=H; $R_2$=Me), m.p. 178°, in an excellent yield Sen-gupta (*J. Indian Chem. Soc.*, 1933, **10**, 343), who prepared this acid by a different method, does not seem to have obtained it in a state of purity. The corresponding triethyl ester on treatment with sodium followed by hydrolysis of the resulting product gives 2 : 3-dimethyl*cyclo*pentan-1-one-3-carboxylic acid (V) as a liquid which has been characterised by the formation of a semicarbazone, m.p. 204°.

$CO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(CN){\cdot}CR(CN){\cdot}CO_2Et$

(IV)



(V)



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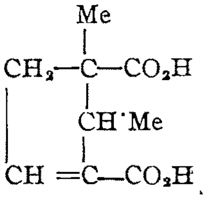
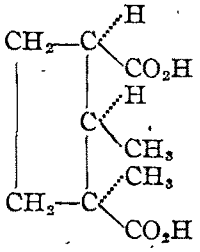
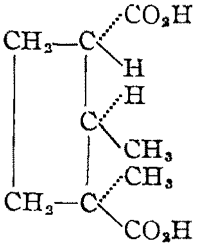


(VII)

The ethyl ester of the keto-acid (V) readily reacts with hydrogen cyanide and the cyanohydrin is dehydrated with phosphoryl chloride and pyridine and the resulting product hydrolysed to give an unsaturated dicarboxylic acid, m.p. 140-45° which probably consists of a mixture of (VI) and (VII). The mixture of unsaturated acids on catalytic hydrogenation in presence of Adam's platinum oxide catalyst affords 2 : 3-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid. Treatment of this acid with acetyl chloride furnishes an anhydride, m.p. 92°, along with a non-separable mixture of isomeric santenic acids (*cf*. Komppa and Rohrmann, *Ber*., 1934, **67 B**, 828). The anhydride on hydrolysis with alcoholic potash gives an acid, m.p. 151-52°.

Obviously, 2 : 3-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid should be capable of existence in two *cis*-forms (VIII) and (IX) and two *trans*-forms (X) and (XI).


(VIII)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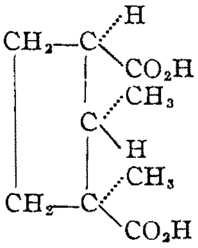
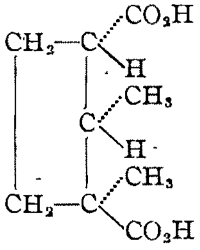

(IX)


(XI)

One of the *cis*-acids, m.p. 171° (anhydride, m.p. 113-14°) was isolated by Aschan by the oxidation of natural santenol or santenone and was designated as santenic acid. Another *cis*-acid, m.p. 151°-52° (anhydride, m.p. 92·5°) was prepared synthetically by Enkvist (*Finska Kem. Medd*., 1932, **41**, 74, 85 ; *J. pr. Chem*., 1933, *ii*, **137**, 261) and Komppa (*Ber*., 1932, **65 B**, 1708), and by Komppa and Rohrmann (*loc. cit*.) using a modification of the Komppa synthesis of camphoric acid. The acid was called allosantenic acid by Enkvist (*loc. cit*.). There can be little doubt that the *cyclo*pentane acid described above is identical with *cis*-allosantenic acid. This, therefore, constitutes an independent synthesis of this interesting acid.

Enkvist (*loc. cit*.) who has studied the stereochemistry of the santenic acids, also succeeded in converting santenic acid and allosantenic acid into their respective *trans*-modifications, m.p. 166-67° and 129-30°, following the universal method of Aschan (*Annalen*, 1912, **387**, 56). According to him *cis*-allosantenic acid should be best represented by (IX) as it yields an anhydride more readily than does the *cis*-santenic acid which should, therefore, be (VIII). The evidence regarding the stereochemical configurations of the isomeric santenic acids is not, however, quite conclusive, since camphoric acid in which one of the *gem*-dimethyl groupings is situated on the same side of the two carboxyl groups (as in VIII) readily furnishes an anhydride. Moreover, the conversion of santenic acid to allosantenic acid which doubtless proceeds through the *trans*-monobromosantenic acid and the related unsaturated acid, santenenic acid (*cf*. Aschan, "*Öfversigt af Finska Vetenskapssocietetens Förhandlingar*", 53A, Nr. 6, 1910) is explained on the basis of formula (XI) which according to Enkvist should in reality represent *trans*-allosantenic acid.

## EXPERIMENTAL

*Ethyl γδ-Dicyano-γ-methylpentane-αδ-dicarboxylate* (IV, R = Me).—Ethyl αβ-dicyano-β-methylbutane-αδ-dicarboxylate was prepared by condensing ethyl laevulate with ethyl cyanoacetate in presence of acetamide and glacial acetic acid and allowing the product obtained to react with hydrocyanic acid (*cf.* Banerjee, *loc. cit.*). The dicyano-ester (18·7 g.) was added to an ice-cold solution of sodium (1·62 g.) in absolute ethyl alcohol (27 c.c.). Methyl iodide (5 c.c.) was then added to it and it was kept overnight. The next day, it was refluxed on the water-bath for 12 hours with the addition of a little methyl iodide from time to time. When cold the product was treated with water and the oil separating was taken up in ether and washed with dilute potassium hydroxide solution to remove traces of iodine. The ether was then evaporated and the residual oil distilled in *vacuo* when ethyl γδ-dicyano-γ-methylpentane-αδ-dicarboxylate (IV, R=Me) was obtained as a colourless mobile liquid boiling at 185°/5mm., yield 18 g. (Found : C, 59·6 ; H, 7·0. $C_{14}H_{20}O_4N_2$ requires C, 60·0; H, 7·1 per cent).

*γ-Methylpentane-αγδ-tricarboxylic Acid* (III, $R_1$=H ; $R_2$=Me).—The methylated product (17·5 g.) was hydrolysed by refluxing on a sand-bath for 16-18 hours with 90 c.c. of concentrated hydrochloric acid The clear solution, thus obtained, was evaporated to dryness on the water-bath and the dry mass extracted with ether. On evaporation of the ether about 13 g. of a partially solid product were obtained. It was dissolved in absolute alcohol (30 c.c ) and concentrated sulphuric acid (3 c.c.) and heated to 110° for 6 hours, a current of hot alcohol vapour being passed through the liquid. The product was diluted with water and extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution and water. The ether was then evaporated and the liquid remaining distilled in *vacuo* when ethyl γ-methylpentane-αγδ-tricarboxylate was obtained as a colourless liquid boiling at 154°/5mm., yield 13 g. (Found : C, 59·6 ; H, 8 6. $C_{15}H_{26}O_6$ requires C, 59·6; H, 8·6 per cent).

The tricarboxylic ester (2 g.) was hydrolysed by heating with concentrated hydrochloric acid (15 c.c.) till a clear solution was obtained. It was then evaporated to dryness on the water-bath and crystallised several times from concentrated hydrochloric acid when pure γ-methylpentane-αγδ-tricarboxylic acid (III, $R_1$=H ; $R_2$=Me) was obtained in colourless crystals, m. p. 178°. (Found : C, 49·2; H, 6·5. $C_9H_{14}O_6$ requires C, 49·5 ; H, 6·4 per cent).

*Ethyl* 2:3-*Dimethyl*cyclo*pentan-1-one-3 : 5-dicarboxylate*.—The tricarboxylic ester (7·5 g.) was heated on the water-bath with molecular sodium (0·69 g ) suspended in dry benzene (18 c c ). Vigorous evolution of hydrogen started on heating and the reaction was complete in 45 minutes. It was then treated with ice-water, and acidified with ice-cold dilute hydrochloric acid The benzene layer was separated, washed well with water and the benzene evaporated completely under reduced pressure. The liquid obtained was then distilled in *vacuo*, b.p. 135°/5mm., yield 4·8 g. It gave a dark violet colouration with alcoholic ferric chloride. (Found : C, 60·6 ; H, 7·6. $C_{13}H_{20}O_5$ requires C, 60·9 ; H, 7·8 per cent).

2:3-*Dimethyl*cyclo*pentan-1-one-3-carboxylic Acid* (V).—The above condensation product (4·5 g.) was hydrolysed by heating on a sand-bath for 6 hours with 50 c.c. of 6% hydrochloric acid. The clear solution, thus obtained, was neutralised with sodium carbonate and extracted with ether to remove any neutral matter present The aqueous solution was then acidified with hydrochloric acid, saturated with salt and extracted with ether. Crude 2:3-dimethyl*cyclo*pentan-1-one-3-carboxylic acid (V) (2·8 g.) was obtained as a liquid. The *semicarbazone* crystallises from water and docomposes at 204° (Found: C, 50 3 ; H, 6·9. $C_9H_{15}O_3N_3$ requires C, 50 7 ; H, 7·0 per cent).

*Ethyl* 2:3-*Dimethyl*cyclo*pentan-1-one-3-carboxylate*.—The keto-acid ( 8 g. )was esterified with absolute alcohol (40 c.c ) and 4 c.c. of alcoholic hydrogen chloride (saturated at 0°), by heating on the water-bath for 8-10 hours. The alcohol was then distilled off and the residue taken up in ether. It was washed with dilute sodium carbonate solution and water, dried over anhydrous calcium chloride and the solvent evaporated. The oil remaining was then distilled at 99°/4mm., yield 8·2 g. (Found: C, 65·0; H, 8·7. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7 per cent).

*Action of Anhydrous Hydrocyanic acid on the Keto-ester* (V).—The above keto-ester (5g.) was added to cold anhydrous liquid hydrocyanic acid prepared from powdered potassium cyanide (10g.) and concentrated sulphuric acid (10 c.c.) diluted with an equal volume of water. The condensation was brought about in presence of a drop of potassium cyanide solution. It was kept overnight at 0° and the cyanohydrin formed was stabilised by adding a drop of concentrated sulphuric acid. Excess of hydrocyanic acid was evaporated off completely at the pump, when the crude cyanohydrin of the keto-ester was obtained.

*Dehydration of the Cyanohydrin and its Ultimate Hydrolysis: Formation of a mixture of Santenenic and* iso*Santenenic Acids*.—The crude cyanohydrin obtained above was heated with phosphorus oxychloride (23 c.c.) and dry pyridine (85 c.c.) at 145-50° for 1 hour. It was then cooled in ice and carefully decomposed with ice-water. The product was acidified with hydrochloric acid and extracted repeatedly with ether. The oil obtained on evaporation of the ether was hydrolysed by heating on a sand-bath for 24 hours with concentrated hydrochloric acid (60 c.c.). When cold the solid insoluble product (2·5 g.) was filtered off. The crude acid melted at 130-40° and even after repeated crystallisations melted at 140-45° and was a mixture of santenenic and *iso*santenenic acids. (Found: C, 58·5; H, 6·5. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5 per cent).

cis-*Allosantenic Acid* (IX).—The above mixture of unsaturated acids (1·01 g.) was dissolved in pure glacial acetic acid (20 c.c.) and shaken with platinum oxide (0·1 g.) in an atmosphere of pure hydrogen under atmospheric pressure and at the room temperature (28°). For the first 10 minutes the absorption was quite rapid, during which time 90 c.c. of hydrogen were absorbed and then the rate suddenly dropped to a very slow but constant value, and for the absorption of the remaining 70 c.c. of hydrogen it took 3 hours. After the absorption was complete it was filtered off and the acetic acid solution was evaporated to dryness on the water-bath. The dry acid (0·85 g.) was treated with acetyl chloride (2 c.c.) and kept overnight. It was then kept in an evacuated desiccator over potassium hydroxide. The liquid residue, thus obtained, was taken up in ether and extracted with dilute sodium carbonate solution to remove acidic impurities. On evaporation of the ether *cis*-allosantenic anhydride was obtained as a crystalline solid. It crystallises readily from petroleum ether in slender needles, m.p. 92° (Found: C, 64·1; H, 7·1. $C_9H_{12}O_3$ requires C, 64·2; H, 7·1 per cent).

The sodium carbonate extract on acidification gave a mixture of isomeric santenic acids which could not be separated.

The pure *cis*-allosantenic acid was obtained by hydrolysing the anhydride with alcoholic potash. It crystallises from water, m.p. 151-52°. (Found: C, 57·7; H, 7·4. $C_9H_{14}O_4$ requires C, 58·0; H, 7·5 per cent).

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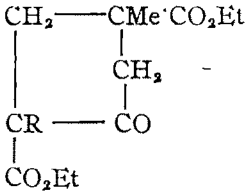
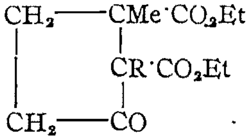
# ACTION OF SODIUM ON ETHYL β METHYLBUTANE-αβδ-TRICARBOXYLATE. PART IV

By Ram Narayan Chakravarti

The Dieckmann condensation product of ethyl β-methylbutane-αβδ-tricarboxylate on treatment with ethyl bromoacetate furnishes ethyl 4-methyl*cyclo*pentan-1-one-2 · 4-dicarboxylate-2-acetate as the only isolable product This on hydrolysis and reduction can be smoothly converted into 1-methyl*cyclo*pentane-1-carboxylic-3-acetic acid, m p. 124-25° An independent synthesis of this latter from ethyl 3-methyl*cyclo*pentan-1-one-3-carboxylate by an adaptation of Ruzicka's method (*Ber.*, 1917, **50**, 1362) is also described

In previous parts of this series (*J. Indian Chem. Soc.*, 1943, **20** 173, 189) it has been shown that the product of the Dieckmann condensation of ethyl β-methylbutane-αβδ-tricarboxylate on alkylation furnishes solely the ester (I) and not the isomeric ester (II).


(I)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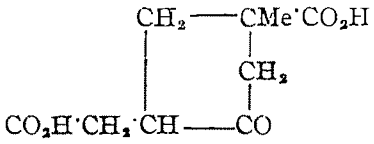
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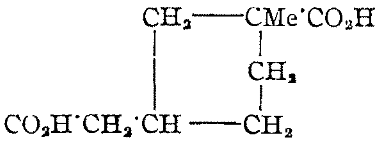
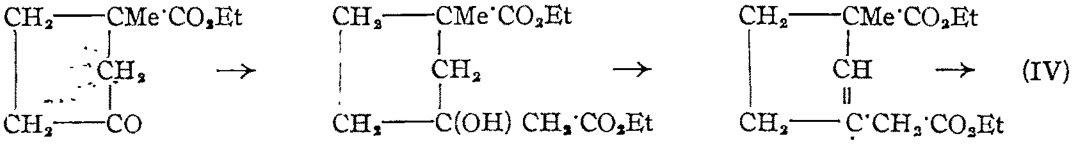
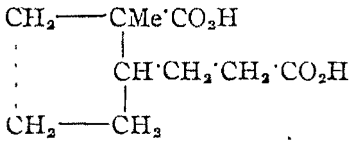

(IV)

In conformity with this view it is now found that the initial sodio derivative formed in the condensation on treatment with ethyl bromoacetate gives ethyl 4-methyl*cyclo*pentan-1-one-2 : 4-dicarboxylate-2-acetate (I, R=$CH_2 \cdot CO_2Et$). The constitution of the latter follows from the fact that on hydrolysis with hydrochloric acid it furnishes 4-methyl*cyclo*pentan-1-one-4-carboxylic-2-acetic acid (III), which has been purified through the ethyl ester, b p. 145°/6 mm. The latter on reduction with amalgamated zinc and concentrated hydrochloric acid according to Clemmensen's method gives 1-methyl*cyclo*pentane-1-carboxylic-3-acetic acid (IV), m p. 124-25°, identical with a synthetic specimen prepared from ethyl 3-methyl*cyclo*pentan-1-one-3-carboxylate (Ruzicka, *Ber.*, 1917, **50**, 1362) through the following stages:



Reference should be made in this connection to the work of Banerjee (*J. Indian Chem. Soc.*, 1940, **17**, 423) who investigated the action of ethyl β-chloropropionate on the sodio derivative described above, and on the basis of Baker's work (*J. Chem. Soc.*, 1931, 1548) formulated the product as (II, R = $CH_2 \cdot CH \cdot CO_2Et$). The latter on successive hydrolysis and reduction is found to give the dicarboxylic acid (V), which on ketonisation according to Dieckmann's method gives a bicyclic ketone which is believed to be 7-methyl-0:3:3-*bicyclo*octane-1-one (VI), since on oxidation with nitric acid it gives impure *trans*-1-methyl*cyclo*pentane-1-carboxylic-2-acetic acid, m.p. 126-27°. Apparently no direct comparison was made with authentic specimens of the *cis*- and *trans*-modifications of 1-methyl*cyclo*pentane-1-carboxylic-2-acetic acid, m. p. 110° and 139° respectively (Linsted and Erington, *J. Chem. Soc*, 1938, 668; also Barnett, Cook and Linsted, *ibid.*, 1935, 1068).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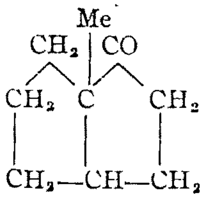
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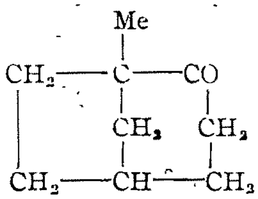
(VII)

There can be little doubt, however, that Banerjee's acid, m.p. 126°, is in reality 1-methyl*cyclo*pentane-1-carboxylic-3-acetic acid, m.p. 124-25°, described above and the bicyclic ketone from which it is formed on oxidation should, therefore, be represented by the alternative formula (VII) and the initial product of the condensation will have the modified formula (I, R = $CH_2 \cdot CH_2 \cdot CO_2Et$).

This brings the above series of reactions into line with the view developed in these series of papers regarding the course pursued by the sodium condensation of ethyl β-methylbutane-αβδ-tricarboxylate. Further work regarding the correctness of the above view of the constitution of the ketone (VII) will shortly be published.

## EXPERIMENTAL

*Ethyl 4-Methyl*cyclo*pentan-1-one-2 : 4-dicarboxylate-2-acetate* (I, R = $CH_2 \cdot CO_2Et$).—Ethyl β-methylbutane-αβδ-tricarboxylate (21·1 g.) was heated on the water-bath for 1 hour with a fine suspension of sodium (2·06 g.) in benzene (50 c.c.). The clear solution, thus obtained, was cooled in ice and ethyl bromoacetate (10 c.c.) added to it and kept overnight. It was then refluxed on the water-bath for 24 hours. When cold the product was treated with water, the benzene layer was separated and the aqueous layer was extracted once with ether. The benzene-ethereal extract was washed with water and the benzene evaporated. The residual oil was then distilled under diminished pressure when ethyl 4-methyl*cyclo*pentan-1-one-2:4-dicarboxylate-2-acetate (I, R = $CH_2 \cdot CO_2Et$) was obtained as a colourless mobile liquid, b.p. 170°/5 mm., yield 21 g. It gave no colouration with alcoholic ferric chloride. (Found : C, 58·5 ; H, 7·3 ; $C_{16}H_{24}O_7$ requires C, 58·5 ; H, 7·3 per cent).

*4'-Methyl*cyclo*pentan-1-one-4-carboxylic-2-acetic Acid* (III).—The above keto-tricarboxylic ester (20 g.) was hydrolysed by refluxing on a sand-bath for 20 hours with concentrated hydrochloric acid (100 c.c.). The oily liquid went into solution in about 2 hours. The solution was evaporated to dryness on the water-bath. The crude acid (12 g.) was heated on the water-bath for 12 hours with absolute alcohol (50 c.c.) and 5 c.c. of alcoholic hydrogen chloride (saturated at 0°). The alcohol was then distilled off. The liquid remaining was treated with water and extracted with ether. The ethereal extract was washed with dilute sodium carbonate solution and water and dried over anhydrous calcium chloride. The solvent was then evaporated and the residual oil distilled under reduced pressure when ethyl 4-methyl*cyclo*pentan-1-one-4-carboxylate 2-acetate (as III) was obtained boiling at 145°/6 mm., yield 10 g. (Found: C, 60·6; H, 7·7. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8 per cent).

1-*Methyl*cyclo*pentane-1-carboxylic-3-acetic Acid* (IV).—Ethyl 4-methyl*cyclo*pentan-1-one-4-carboxylate-2-acetate (5·5 g.) was heated on a sand-bath for 30 hours with concentrated hydrochloric acid (45 c.c.) and zinc (60 g.) previously amalgamated by keeping in contact with 5% mercuric chloride solution for an hour. More hydrochloric acid (50 c.c. in all) was added from time to time. The clear solution was saturated with salt and extracted repeatedly with ether. The ethereal solution was washed with water and the ether was then evaporated. The residual liquid for the most part solidified on keeping in a vacuum desiccator. It was filtered at the pump and washed with cold water. The residue after one crystallisation from water melted at 116-17° but after several crystallisations the melting point rose up to 124-25° and did not change on further crystallisations. Moreover, the mixed melting point of this acid with a sample of the same acid, prepared as described below, by a modification of Ruzicka's method (*loc. cit.*), was also 124-25°. (Found: C, 57·7; H, 7·5. $C_9H_{14}O_4$ requires C, 58·0; H, 7·5 per cent).

*Synthesis of* 1-*Methyl*cyclo*pentane-1-carboxylic-3-acetic acid* (IV) (by a modification of Ruzicka's method).—The mixture of unsaturated and hydroxy esters as obtained by the condensation of ethyl bromoacetate with ethyl 3-methyl*cyclo*pentan-1-one-3-carboxylate (5 g.) in presence of zinc was heated on the water-bath for 3 hours with ⅓ molecule of phosphorus oxychloride and 3 volumes of dry benzene. It was then treated with ice-water, the benzene layer was separated and the aqueous layer extracted with ether. The benzene-ethereal extract was washed with dilute sodium carbonate solution and water and the solvent was then evaporated. A mixture of the unsaturated esters was obtained, boiling at 125°/4 mm., on distillation of the residual oil, yield 2·5 g.

The mixture of unsaturated esters (2·5 g.) was dissolved in absolute alcohol (16 c.c.) and shaken in an atmosphere of pure hydrogen at the room temperature and under atmospheric pressure in presence of platinum oxide (0·2 g.) till the absorption of hydrogen was complete. In half an hour 80% of the calculated amount of hydrogen was absorbed, and it took 16 hours for the absorption of the rest. The alcoholic solution was then filtered and the alcohol evaporated. The residual liquid was hydrolysed by heating on the water-bath for 2 hours with excess of 10% aqueous alcoholic caustic potash. The alcohol was then evaporated with the addition of water and the solution was acidified with hydrochloric acid and extracted repeatedly with ether. On evaporation of the ether a liquid residue was obtained which solidified partly on keeping in a vacuum desiccator. It was filtered at the pump and washed with a little cold water. The solid product, thus obtained, on crystallisation from water melted at 116-18° (as described by Ruzicka) but after three crystallisations attained a constant melting point, 124-25°.

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# COMPLEX COMPOUNDS OF BIGUANIDE WITH BI- AND TERVALENT METALS. PART VI. COPPER, NICKEL AND COBALT (*ic*) PHENYLBIGUANIDE-*p*-SULPHONIC ACID

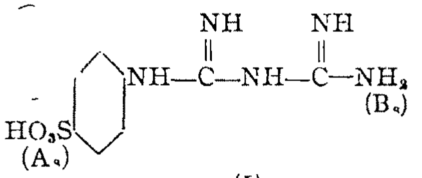
By Priyadaranjan Rây and Sushil Kumar Siddhanta

A new derivative of biguanide, phenylbiguanide-*p*-sulphonic acid, has been prepared from sulphanilic acid and dicyandiamide. The substance behaves as an ampholyte and forms stable complexes with bivalent copper and nickel, as well as with tervalent cobalt. These complexes themselves behave as ampholytes and are insoluble in water. Co-ordination with copper and nickel is found to increase slightly the strength of the acid group of the ampholyte, while co-ordination with cobalt (*ic*) increases the strength of both the acidic and the basic groups.

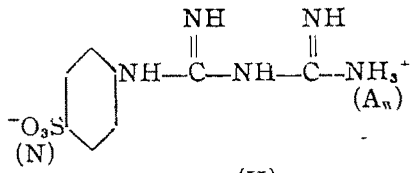
In a series of papers Rây and co-workers (*J. Indian Chem. Soc.*, 1937, **14**, 671; 1938, **15**, 347, 350, 353; 1939, **16**, 617, 621, 629; 1941, **18**, 217, 239, 298, 609; 1942, **19**, 1) have described a large number of complex compounds of biguanide and its substitution products with bi- and tervalent metals like Cu, Ni, Pd, Cr and Co.

A new substituted biguanide, phenylbiguanide-*p*-sulphonic acid (I), has now been prepared and the present paper deals with the preparation, properties and the constitution of this derivative and its complex compounds with copper, nickel and cobalt.

Phenylbiguanide-*p*-sulphonic acid (I) exists evidently in the form of a *zwitter ion* (II), as both the acidic and basic groups in (I) are quite strong, while the corresponding conjugate basic and acidic groups in (II) are respectively neutral and weak.



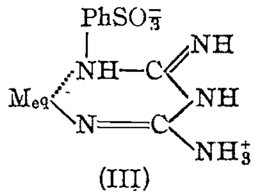
(I)



(II)

[$A_s$ = strong acid, $B_s$ = strong base, $A_w$ = weak acid, N = neutral]

The substance is, therefore, practically insoluble in water due to internal salt formation. Hence the complex compounds of this biguanide derivative with metallic elements were expected to be quite insoluble in water, resembling the inner metallic complexes and themselves behaving as ampholytes. These properties have been actually realised in the complexes described here. The study of such ampholytic complexes has got an additional interest of its own, as co-ordination with the metal atom might influence the strength of the acidic and basic groups of the molecule. It has been found that co-ordination with copper and nickel increases the acid character of the ampholyte, while that with cobaltic cobalt enhances somewhat the strengths of both the cationic acid and the anionic base, as demonstrated by the relative solubility of these complexes in alkalis and acids respectively.



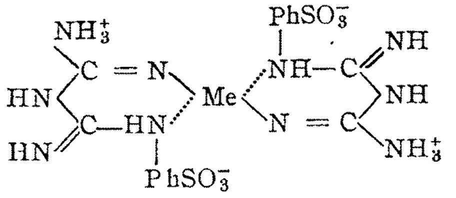
(III)

where $M^{eq} = \frac{1}{2}\,Cu^{++}$, $\frac{1}{2}\,Ni^{++}$, or, $\frac{1}{3}\,Co^{+++}$.

In a line with the constitution of metal biguanide complexes in general, the structure of the phenylbiguanide-*p*-sulphonic acid complexes can be represented by (III).

These complexes are soluble in ammonia and alkalis without decomposition, but are insoluble in water or alcohol. The cobalt complex dissolves unchanged in dilute acids also.

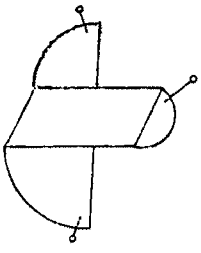
The four co-ordinated metal complexes of copper and nickel are likely to exhibit *cis-trans* isomerism due to planar configuration (*cf.* Rây and Chakravarty, *J. Indian Chem. Soc.*, 1941, **18**, 609). But only one form, probably the *trans* (IV) of the copper and nickel phenylbiguanide, *p*-sulphonic acid, could be obtained in spite of all variations in their methods of preparation. The *cis* form seems to be unstable, due, evidently, to the close proximity which the two negative $PhSO_3^-$ groups would assume in the molecule.



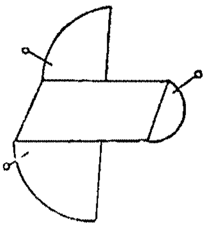
(IV, *trans*)

The octahedral cobaltic complex with (I) might also exist in three geometrically isomeric forms as indicated by V, VI and VII, of which the last (VII) with three $PhSO_3$ groups away from one another should represent the most stable form.

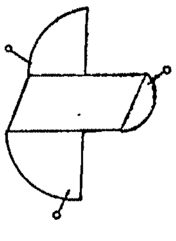
The dot with bar indicates the position of $PhSO_3^-$ groups.



(V)



(VI)



(VII)

## EXPERIMENTAL

*Phenylbiguanide-p-sulphonic Acid.*—Sulphanilic acid (2 g.), dicyandiamide (1·2 g.) and 30 c.c. of water were refluxed on a free flame for about 2 hours, when a silky, white solid separated out. This was filtered after cooling and washed with water. For purification it was dissolved in ammonia and reprecipitated by dilute HCl. {Found . N, 26·90 ; S (by peroxide fusion), 12·60. $HO_3S{\cdot}C_6H_4{\cdot}C_2N_5H_8$ requires N, 27·20 ; S, 12·45 per cent}.

The substance forms silky white crystals, very slightly acid to litmus. It is insoluble in cold water and organic solvents like alcohol, ether, acetone, etc., but soluble in strong acids as well as in dilute alkalis and ammonia, m p. (decomp.), 265-68°.

*Copper Phenylbiguanide-p-sulphonic Acid.*—A solution of $CuSO_4$, $5H_2O$ ( 1 g. ) was added to a solution of phenylbiguanide-*p*-sulphonic acid (2·05 g.) in excess of ammonia at a temperature of 50-60°. Violet crystals separated on cooling. These were filtered, washed first with water, then with alcohol and finally dried in air. {Found : N, 23·66 ; Cu, 10·61, 10·64 ;

$H_2O$ (loss at 90°), 3·0. [$Cu(BigPhSO_3H)_2$], $H_2O$ requires N, 23·59 ; Cu, 10·71 ; $H_2O$, 3·04 per cent}. $HO_3S$ PhBigH = one molecule of phenylbiguanide-*p*-sulphonic acid.

The substance forms violet crystals, insoluble in water and alcohol, but dissolves readily in alkalis and ammonia. It is neutral to litmus and dissolves with decomposition in acetic acid and dilute mineral acids.

*Nickel Phenylbiguanide-*p*-sulphonic Acid.*—A solution of 2·2 g. of phenylbiguanide-*p*-sulphonic acid in ammonia was mixed with a solution of 1 g. of $NiCl_2$, $6H_2O$ and the mixture was heated on the water-bath until yellow crystals appeared. These were washed and dried as before. {Found : N, 23·14 ; Ni, 9·59 ; $H_2O$ (loss at 90°), 6·08. [$Ni(BigPhSO_3H)_2$], $2H_2O$ requires N, 23·07 ; Ni, 9·67 ; $H_2O$, 5·93 per cent}.

The substance forms yellow crystals, insoluble in water or alcohol, but dissolves freely in alkalis and ammonia. It is not affected by very dilute mineral acids or 2*N* acetic acid, but dissolves in stronger acids with decomposition. It reacts neutral to litmus.

*Cobaltic Phenylbiguanide-*p*-sulphonic Acid.*—Phenylbiguanide-*p*-sulphonic acid (3·3 g.) in ammoniacal solution was added to an aqueous solution of 1 g. of $CoCl_2$, $6H_2O$ and a vigorous current of air was passed through the mixture till it was practically free from ammonia. The insoluble product was dissolved with addition of fresh ammonia and the solution filtered. The filtrate was evaporated on the water-bath to remove the major quantity of ammonia. The mixture was cooled and allowed to stand overnight in the cold. The red crystals that separated were washed and dried as usual. {Found: N, 22·76 ; Co, 6·33 ; $H_2O$ (loss at 90°), 9·96. [$Co(BigPhSO_3H)_3$],$5H_2O$ requires N, 22·90 ; Co, 6·42 ; $H_2O$, 9·82 per cent}.

The substance forms red crystals, neutral to litmus. It is only slightly soluble in cold water, but more in hot water. The substance behaves as an ampholyte and dissolves readily in acids, alkalis and ammonia without decomposition.

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# RECOVERY OF ELEMENTARY SULPHUR FROM GASES CONTAINING SULPHURETTED HYDROGEN

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For the recovery of elementary sulphur from waste gases, action of iron oxide as adsorbent for $H_2S$ has been tested Incorporation of $Al_2O_3$ and $MnO_2$ has been found to increase the activity of the adsorbent

India's consumption of sulphur in normal times was of the order of 30,000 tons per year and it has been estimated that about 10,000 tons (*i.e.*, one third of the total consumption) of recoverable sulphur are lost annually in the various coke-ovens in India. In view of the position of sulphur in India and its great economic importance in industrial operations, it was thought desirable to investigate the possibility of recovering elementary sulphur from these gases (which are normally poor in sulphurous constituents).

Development of the newer wet processes for the purification of these gases (*e.g.*, Thylox process using alkaline solution of arsenious oxide, Gluud's still process using ferric hydroxide mud, Otto process using ferricyanides, Gorbitol process using mono- and triethanolamine, Phenolate process using alkaline solution of phenols, etc.), has not been able to do away with the dry processes involving the use of oxide of iron, luxmasses, activated carbon etc. In the case of gases comparatively poor in $H_2S$ content, the dry processes are generally utilised. These processes, are, therefore, of special importance in India where the coals and consequently the industrial gases, are, on the whole, poorer in sulphur content (Assam and Punjab coals have, however, high content of sulphur).

In the present investigation, we have studied the action of iron oxide as adsorbing agent for $H_2S$ and have been able to increase its activity by incorporating *alumina* or *oxide of manganese*. Adsorbing capacity of activated carbon was also found to increase by incorporating it with *alumina*. Though the activity of activated carbon was found to be somewhat less than either of *alumina and iron oxide* and *oxide of manganese and iron oxide*, it can be used effectively in the case of gases containing organic sulphur. The amount of sulphur actually recovered by extraction from various adsorbing agents has been determined and the adsorbents have, then, been revivified to almost their original activity.

## EXPERIMENTAL

For this study, an artificial mixture of the following composition by volume, was used

$$H_2 = 50\% \ ; \quad CO = 45\% \ ; \quad H_2S = 2 \text{ to } 3\% \ ; \quad N_2 = \text{traces} \ ; \quad O_2 = \text{traces}.$$

*Preparation of Adsorbents.*—The various adsorbents were prepared as follows:—

1. Ferric hydroxide, prepared by adding 1·5*N*-ammonia solution to ferric chloride solution containing 6·3 g. of $Fe_2O_3$ per 100 c.c.

2. Mixed $Fe_2O_3$—$Al_2O_3$ adsorbent was obtained by mixing various proportions of aluminium sulphate solution containing 4·95 g. of $Al_2O_3$ per 100 c.c., to a fixed amount of the above mentioned ferric chloride solution and precipitating the same by 1·5*N*-ammonium hydroxide.

3. Mixed $Fe_2O_3$—$MnO_2$ adsorbent was prepared as above. Manganese sulphate containing 10·97 g. of $MnO_2$ per 100 c c. being taken in place of aluminium sulphate.

4. Mixed activated carbon (Kahlbaum)—$Al_2O_3$ was prepared by suspending 10 to 15 g. of activated carbon in the aluminium sulphate solution and precipitating the same by stock ammonia solution.

5. Mechanical mixtures of different adsorbents were made by mixing different amounts of constituents intimately in a mortar.

In all the above cases the adsorbents, before each experiment, were maintained at particle size of 4·5 mm. to 3 mm.

*Procedure.*—The experimental gas was collected in an aspirator bottle over concentrated solution of sodium chloride, from which it was passed through dry fused calcium chloride. The passage was regulated with a screw clip and the gas passed through three **U**-tubes in series containing definite quantities of adsorbents. The gas was then passed through two guard vessels and finally bubbled through dilute solution of lead acetate. The passage of gas was stopped as soon as the colouration was seen in lead acetate vessel and the first **U**-tube weighed in order to find out the amount of sulphuretted hydrogen adsorbed. A fresh tube charged with adsorbent was introduced in place of the third **U**-tube at the end of the series so that the middle tube came in place of the first and was saturated before being weighed. In this way the saturation point of the adsorbent with regard to $H_2S$ was found out. The following tables give the results of preliminary investigations.

TABLE I

Adsorbent used:—Mechanical mixture of $Fe_2O_3$ and $Al_2O_3$ dried at 95° to 100° in a current $Fe_2O_3$ of dry air for 1½ hrs. Rate = 20 bubbles per minute. $H_2S$ in gaseous mixture = 2·4% by volume.

| $Al_2O_3$ in the adsorbent. | Sulphur content | | $Al_2O_3$ in the adsorbent. | Sulphur content | |
|---|---|---|---|---|---|
| | Average increase in wt. | Sulphur estimated by fusion method. | | Average increase in wt. | Sulphur estimated by fusion method. |
| 0% | 25·55% | 25·70% | 37·5% | 28·03% | 28·10% |
| 11·5 | 25·987 | 25·90 | 41·2 | 24·02 | 24·00 |
| 20·1 | 35·03 | 34·80 | 60·0 | 17·45 | 17·00 |
| 28·5 | 30·935 | 31·11 | 100 | 0·395 | 0·36 |
| 33·3 | 29·04 | 29·50 | | | |

TABLE II

Adsorbent used.—Mechanical mixture of $Fe_2O_3$ and $MnO_2$, dried at 95° to 100°. $H_2S$ in the gas = 2·91% by vol.

| $MnO_2$ in the mixed adsorbents | Sulphur content | |
|---|---|---|
| | Average increase in wt. | Sulphur estimated by fusion method. |
| 0% | 25·55% | 25·70% |
| 7 | 27·4 | 27·12 |
| 13 | 32·05 | 31·79 |
| 20 | 29·47 | 29·15 |
| 100 | 2·20 | 2·11 |

It will be observed that addition of 20·1% $Al_2O_3$ or 13% $MnO_3$ increases the amount of adsorption of $H_2S$ in $Fe_2O_3$ from 25·7 to 34·8% or 31·79%.

## *Optimum Composition of Mixed Adsorbents*

Mixed adsorbents, prepared by simultaneous precipitation of $Fe_2O_3$ and $Al_2O_3$ from solution, are likely to give better results. Moreover, the water content in the adsorbent at the time of its use is likely to prove an important factor in the adsorption.

The following results were obtained when experiments were performed with a view to finding out the optimum composition of various mixed adsorbents and their optimum temperature of activation.

TABLE III

Adsorbent used : $Fe_2O_3$ and $Al_2O_3$, formed by simultaneous precipitation, and activated at 230-35° for 1½ hours, $H_2S$ in gaseous mixture being 2·65% by volume.

| $Al_2O_3$ in adsorbent | Sulphur content: Average increase in wt. | Sulphur content: Sulphur estimated (fusion method). |
|---|---|---|
| 0·0% | 25 54% | 25·70% |
| 19 47 | 48·06 | 47 82 |
| 25 11 | 56·98 | 56 83 |
| 29·83 | 54·80 | 54·10 |
| 38·79 | 52·61 | 51·68 |
| 100·0 | 0·395 | 0·36 |

TABLE IV

Adsorbent used: Mixed adsorbent containing $Fe_2O_3$ and $MnO_2$ obtained by simultaneous precipitation, and activated at 230-35° for 1½ hrs., $H_2S$ in the gaseous mixture being 2·12% by volume.

| $MnO_2$ in the mixed adsorbents. | Sulphur content: Average increase in wt. | Sulphur content: Sulphur estimated by fusion method. |
|---|---|---|
| 0·0% | 25 55% | 25·7 % |
| 20·30 | 44·31 | 43·46 |
| 30·84 | 47 98 | 47·18 |
| 34 82 | 54·72 | 53 98 |
| 40 10 | 52 09 | 52·00 |
| 100 | 2·20 | 2·11 |

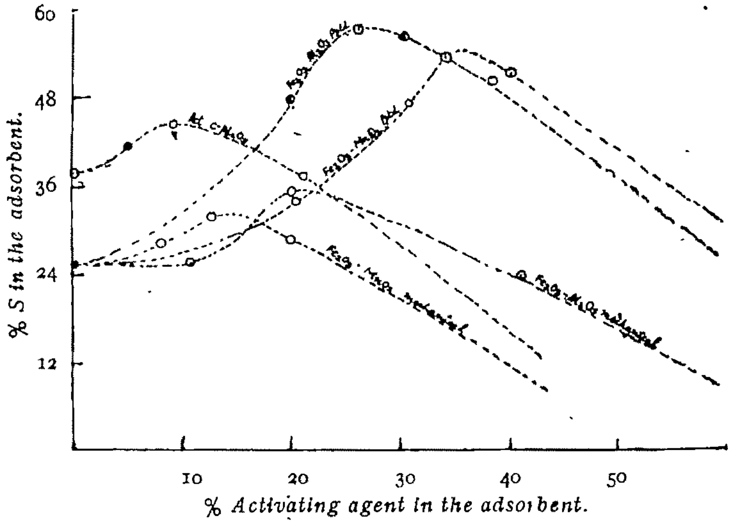
TABLE V

Adsorbent used : Activated charcoal incorporated with $Al_2O_3$, temperature of activation being 230-35°, the percentage of $H_2S$ being 2·43 by volume.

| $Al_2O_3$ in the mixed adsorbents. | Sulphur content: Average increase in wt. | Sulphur content: Sulphur estimated by Eschka method. |
|---|---|---|
| 100·0% | 0 395% | 0 36% |
| 18·88 | 41·80 | 37 72 |
| 14·20 | 42 40 | 39 24 |
| 9 28 | 48 67 | 43 98 |
| 4 85 | 45·47 | 41·12 |
| 0 | 43·67 | 38·28 |

It will be seen that in the case of all the adsorbents used, incorporation of $Al_2O_3$ had decidedly an augmenting effect, the increase being maximum in the case of $Fe_2O_3$ and $Al_2O_3$. The use of $Fe_2O_3$ for the purification of coal gas is well known. But the augmenting effect of $Al_2O_3$ seems to have remained unnoticed—while pure $Fe_2O_3$ shows an adsorption of 25·54% only and pure $Al_2O_3$ only 0·36%—a mixed adsorbent containing 25·11% $Al_2O_3$ shows 56·98% increase in weight due to adsorption of $H_2S$. An estimation of sulphur in the adsorbent shows that the increase in weight is not due to any foreign substance. It may be noted (Table X) that a maximum amount of sulphur was extracted by solvents from $Fe_2O_3-Al_2O_3$ adsorbent.

FIG. 1



It was thought that incorporation of an oxidising agent like $MnO_2$ with $Fe_2O_3$ might give even better results than $Al_2O_3$. This expectation has not, however, materialised.

In the case of activated charcoal incorporated with alumina, the adsorption was lower than either of $F_2O_3-Al_2O_3$ or $Fe_2O_3-MnO_2$. In view of the fact that activated carbon is capable of adsorbing $H_2S$ from gases containing traces of this gas and its ability to adsorb organic sulphur (*Chem. Fabric*, 1939, **12**, 23), the action of this mixed adorbent has been further investigated.

Results of Tables I, II, III, IV and V are compared in Fig 1.

### *Activation of Various Adsorbents*

It will be seen from previous results that lower adsorption is obtained with samples dried below 100°, whereas much higher adsorption is obtained with samples heated to 230°-235°. Evidently moisture plays an important part in determining the activity. The necessity of traces of moisture for adsorption has been noted by various investigators working with silica gel, alumina gel and other adsorbents. In the case of iron oxide ore used for gas refining Avery (*Gas J.*, 1931, **196**, 311) maintains that best results can be obtained with samples containing 35-40% moisture while Thomson (*Gas J.*, 1940, **229**, 190) recommends 20-25% moisture for the same purpose. The adsorbents used by us have, therefore, been preheated to various temperatures in order to regulate moisture content and their activity determined.

About 15 to 20 g. of the sample were taken in a glass combustion tube which was maintained at the particular temperature for 1½ hours. Dry air was blown in with a Cenco blower through this electrically heated tube at a constant rate. Results are represented in Figs. 2 and 3.

TABLE VI

Adsorbent: $Fe_2O_3-Al_2O_3$, containing 25·11% of $Al_2O_3$, obtained by simultaneous precipitation. Time of activation = 1½ hours. $H_2S$ = 2·81% by volume

| Temp. | Water content | Sulphur content | |
|---|---|---|---|
| | | Average increase in weight | Sulphur estimated by fusion method |
| 95° | 13·48% | 27·40% | 27·06% |
| 200° | 8·01 | 52·91 | 51·72 |
| 240-245° | 6·86 | 60·34 | 59·88 |
| 300° | 4·98 | 54·93 | 54·20 |
| Strong ignition | — | 41·95 | 40·23 |

In view of the success achieved by $Fe_2O_3-Al_2O_3$ mixture, we thought it advisable to investigate the action of bauxite as an adsorbent. For this purpose, two samples of bauxite, obtained through the courtesy of the Director, Geological Survey of India, were studied.

FIG. 2

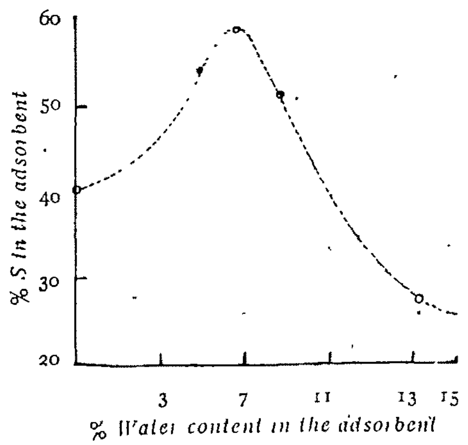
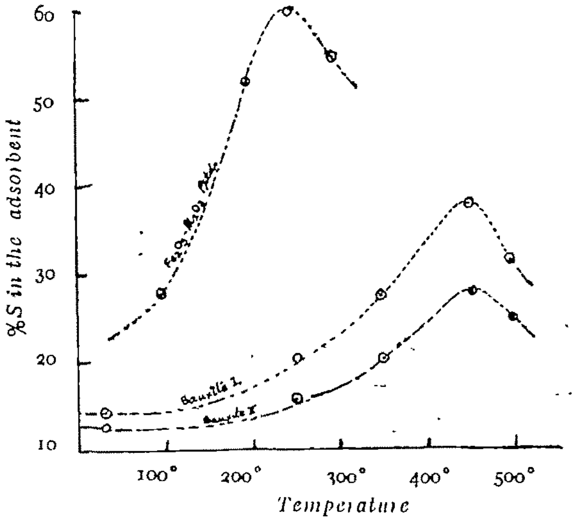


FIG. 3



### TABLE VII

*Bauxite*

*Analysis*

| | Sample I. | Sample II. |
|---|---|---|
| Loss on ignition (%) | 20·32 | 20·9 |
| $Al_2O_3$ | 27·8 | 65 2 |
| $Fe_2O_3$ | 11 7 | 1 9 |
| $SiO_2$ | 11·6 | 0·34 |
| $TiO_2$ | 6·7 | 11 3 |
| CaO | 20·8 | Traces |
| MgO | 0 41 | Traces |

*Time of activation (1½ hrs.)*

| | Sample I ($H_2S$ in gas =2·73%) | | Sample II ($H_2S$ in gas =2·88%) | |
|---|---|---|---|---|
| Temp. | Sulphur content | | Sulphur content | |
| | Average increase in wt. | Sulphur estimated. | Average Increase in wt. | Sulphur estimated. |
| 30-31° | 15 48% | 14·88% | 13·10% | 12·62% |
| 250° | 21·48 | 20·05 | 17·23 | 16·28 |
| 350° | 27·26 | 27·10 | 20 12 | 20 01 |
| 450° | 37·49 | 37·12 | 27·71 | 27 58 |
| 500° | 31·22 | 31·22 | 25·83 | 24·98 |

Comparatively low figure of adsorption in the case of these bauxites is perhaps due to a low $Fe_2O_3$ content in the samples and a comparatively high $Al_2O_3$ content. Thus sample II with higher $Al_2O_3$ and lower $Fe_2O_3$ content than sample I shows a lower adsorption.

It will be seen that the optimum results have been obtained by heating precipitated *iron oxide-alumina* to 240 250° and bauxite to 450°. In the case of bauxite, the organic constituents and excess of moisture have to be removed by heating it to a higher temperature *i.e.* 450°.

*Time of contact of the different adsobents* was determined and the results are stated below.

### TABLE VIII

*Optimum rate of flow*

**A.** $Fe_2O_3-Al_2O_3$ with 25·11% $Al_2O_3$, activated at 230-235° for 1½ hours. $H_2S$ =3·01% by volume.

**B.** $Fe_2O_3-MnO_2$ with 30·84% $MnO_2$ activated at 230-235° for 1½ hours. $H_2S$= 3·1% by volume.

**C.** Activated carbon—$Al_2O_3$ with 14·2% $Al_2O_3$, activated at 230-235°. $H_2S$= 2·62% by volume.

| | A. Sulphur content | | B. Sulphur content | | C. Sulphur content | |
|---|---|---|---|---|---|---|
| Rate of flow (bubbles per min.) | Average increase in wt | Sulphur estimated by fusion method | Average increase in wt | Sulphur estimated. | Average increase in wt. | Sulphur estimated. |
| | | | 48·26% | 48·10% | 42·20% | 37·80% |
| 20 | 55·04% | 54 85% | 47 94 | 47·28 | 41·85 | 37 70 |
| 30 | 54 99 | 54 25 | 46·08 | 46·00 | 38 61 | 36·15 |
| 40 | 54 92 | 54·13 | 45·47 | 45·30 | 35 77 | 34·00 |
| 60 | 53·99 | 53·78 | 39·87 | 39·10 | 31·60 | 28·06 |
| 80 | 50·95 | 50·05 | | | | |

The relative merits of the different adsorbents can be had from a comparison of the above tables.

### *Effect of Oxygen present in the Gaseous Mixture*

Though adequate quantities of air when mixed with sulphurous industrial gases passing through iron-oxide bed are known to give better results, excess of oxygen may have harmful effect in that it may cause fusion of sulphur, thereby closing the pores of the adsorbent or even ignition of the gas. Experiments were, therefore, done to get an idea of the optimum proportion of oxygen under a given set of condition. Results are given below.

TABLE IX

Adsorbent used : $Fe_2O_3-Al_2O_3$ with 29·83% $Al_2O_3$, activated at 230-235° for 1½ hrs. $H_2S$ in the gaseous mixture being 2·06% by volume.

| Oxygen (by volume). | Sulphur content<br>Average increase in wt. | Sulphur estimated. |
|---|---|---|
| 1·56% | 54·94% | 54·24% |
| 2·38 | 55·25 | 55·12 |
| 3·10 | 58·68 | 58·13 |
| 4·20 | 58·72 | 58·15 |
| 5·05 | 58·88 | 58·20 |

The reason for increase of adsorption at 3 to 5% oxygen content is evidently regeneration of iron oxide *in situ* with the liberation of free sulphur.

### *Recovery of Elementary Sulphur from Adsorbents*

Modern processes usually recover sulphur from the spent oxide by extraction with $CS_2$ (Broche & Net. *Brennst.-Chem.*, 1932, **13**, 201, 664). The various adsorbents used by us were, therefore, extracted with carbon disulphide and the elementary sulphur was estimated by evaporation of the solvent.

As combined sulphur is not extracted, we have passed air through the residue after each extraction. The residue was transferred to glass combustion tube and air was passed through it for one hour at the rate of 100 bubbles per minute at room temperature. This would liberate any combined sulphur and would increase the amount of extractable sulphur. The sulphur obtained by extraction is yellowish and is quite pure. Extraction was carried out at ordinary pressure in a Soxhlet and at higher pressure in an autoclave—a higher yield being obtained when pressure is applied. Results are shown below.

TABLE X

*Extraction by carbon disulphide*

| Particulars of adsorbents. | Sulphur in adsorbents. | Manner of extraction. | Sulphur content (%)<br>Before aeration. (1st Extract) | After 1st aeration. (2nd Extract) | After 2nd aeration. (3rd Extract) | Total. |
|---|---|---|---|---|---|---|
| $Fe_2O-Al_2O_3$ (20·1%) Mechanical mixture | 34·8% | (*a*) Soxhlet | 84·3 | 4·0 | 1·1 | 89·4 |
| | | (*b*) Autoclave (4·5 kg.) | 96·7 | — | — | 96·7 |
| $Fe_2O_3-Al_2O_3$ (25·11%) Precipitated from soln. | 56·83 | (*a*) Soxhlet | 79·10 | 2·48 | 1·17 | 82·75 |
| | | (*b*) Autoclave (4·5 kg.) | 93·10 | 0·56 | — | 93·66 |
| $Fe_2O_3-Al_2O_3$ (25·11%) Precipitated and activated at 240-245° | 59·88 | (*a*) Soxhlet | 76·82 | 3·10 | 0·5 | 80·42 |
| | | (*b*) Autoclave (4·5 kg.) | 90·67 | 0·20 | — | 90·87 |
| $Fe_2O_3-MnO_2$ (34·82%) Precipitated from soln | 53·98 | (*a*) Soxhlet | 81·22 | 2·50 | 0·82 | 84·54 |
| | | (*b*) Autoclave (4·5 kg.) | 93·86 | 0·10 | — | 93·96 |
| Activated carbon-$Al_2O_3$ (9·28%). | 43·98 | (*a*) Soxhlet | 61·10 | 1·10 | — | 62·20 |
| | | (*b*) Autoclave (4·5 kg.) | 68·2 | 0·1 | — | 68·3 |
| Bauxite—Sample I | 37·12 | (*a*) Soxhlet | 22·21 | 1·80 | — | 24·01 |
| | | (*b*) Autoclave (4·5 kg.) | 28·22 | — | — | 28·22 |

It will be found that the extraction of elementary sulphur is quite satisfactory in the cases of $Fe_2O_3-Al_2O_3$ and $Fe_2O_3-Mn_2O_3$. This evidently is due to the formation of free sulphur ; the traces of oxygen present in the gas oxidise sulphuretted hydrogen in the presence of alumina, liberating free sulphur which can easily be extracted. A small amount of sulphur adheres, however, tenaciously to the absorbent and can only be extracted when pressure is employed. The same remarks apply to $Fe_2O_3-MnO_2$ adsorbent, free elementary sulphur being present in the substance after the passage of the gas.

In the case of activated carbon—alumina, the amount extracted does not seem to be very satisfactory and is 62·2% at ordinary and 68·3% under high pressures. This is due, either to the unsuitability of activated carbon used by us for the purpose or to the sulphur being difficultly extractable. It will be seen that aeration does not appreciably increase the amount of extractable sulphur. In the case of bauxite, only a small percentage of sulphur is extractable with carbon disulphide It is likely that substances like calcium and magnesium present in bauxite, form stable compounds of sulphur which cannot be extracted. In the case of the three samples of $Fe_2O_3-Al_2O_3$ adsorbent extracted, it will be noticed that there is a gradual fall in the extraction value with the increase in the percentage of sulphur in the adsorbent. Evidently, the higher the sulphur content in the $Fe_2O_3-Al_2O_3$, the lower is the proportion of extracted sulphur. It is probable that in the presence of excess of sulphur, complex sulphides of the type $(Fe\,S_2, FeS)_X\,(H_2O)_Y$ are formed which are more stable than simple sulphides and liberate sulphur with difficulty.

## *Revivification of the Adsorbents*

Utility of an adsorbent on an industrial scale will depend to a great extent on whether or not the adsorbent can be revivified to its original activity.

(*a*) $Fe_2O_3-Al_2O_3$ *adsorbent*.—Stinnes (B.P. 371,117) patented a process for restoring used spent oxide to its former activity by the addition of small quantity of alkaline earth salts. Taking the clue from the above brief report, we have been able to restore $Fe_2O_3-Al_2O_3$ adsorbent after extraction to almost its original activity.

The adsorbent which contained 56·98% sulphur and was extracted under pressure with $CS_2$, was intimately mixed with different quantities of calcium carbonate and the mixture heated to a temperature of 230 − 235° in a current of dry air for 1½ hours. The activity, determined in the usual manner, is shown in Table XI.

TABLE XI

*Revivified* $Fe_2O_3-Al_2O_3$ *adsorbent.*
$H_2S$ in gas = 2·63% by volume.

| $CaCO_3$ used. | Sulphur content<br>Average increase in weight | <br>Sulphur estimated by fusion method. |
|---|---|---|
| 0 | 45·59% | 45·13% |
| 4% | 50·93 | 50·16 |
| 6 | 55·96 | 55·71 |
| 8 | 55·73 | 55·68 |

TABLE XII

*Sulphur from revivified* $Fe_2O_3-Al_2O_3$ *adsorbent.*
Sulphur content in the adsorbent = 55·71%.

| Manner of extraction. | Percentage of sulphur<br>Before aeration | <br>After first aeration. | <br>Total. |
|---|---|---|---|
| Soxhlet | 80·50 | 3·20 | 83·70 |
| Autoclave (4·5 kg.) | 93·70 | ... | 93·70 |

The data shown in Table XII will further show that extraction of sulphur from this revivified mass is quite satisfactory and is practically of the same order as the original.

(*b*) *Activated carbon*—$Al_2O_3$ *adsorbent*.—In this case, the used charcoal, after extraction with carbon disulphide was revivified with steam, air and traces of ammonia mixture at a temperature of 250°. This method of activating charcoal was recommended by Bakes, King and Sinnatt (*D. S. I. R., Fuel Res. Tech. Paper*, No. 31, 1931). The best results were obtained after passing the above gases for a period of 60 minutes as the following table shows.

TABLE XIII

*Revivification of activated carbon*—$Al_2O_3$ *adsorbent containing* 9·28% $Al_2O_3$

Sulphur in the adsorbent=43.98%. $H_2S$ in the gas=2.28 %by vol. Rate of passing the mixed gases=100 bubbles per min.

| | Sulphur content | |
|---|---|---|
| Period of revivification. | Average increase in weight. | Sulphur estimated by Eschka method. |
| 0 | 25·74% | 23·24% |
| 45 mins. | 38·50 | 38·10 |
| 60 | 43·53 | 43·21 |
| 75 | 43·45 | 43·15 |

It will be seen that the original activity is fully restored, the loss in weight during revivification being negligible. It is likely that steam and air act as sweeping or washing out agents and ammonia removes any sulphur compound in the adsorbent by chemical action. A small amount of sulphur compounds retained by the adsorbent is, however, lost during the process.

Our thanks are due to Dr. K. M. Chakravarty for various suggestions in carrying out the investigation.

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# THE MECHANISM OF THE ACTION OF CHARCOAL ON POTASSIUM NITRATE. PART II. STUDY OF THE REACTIONS

By Trambaklal Mohanlal Oza and M. S. Shah

A detailed study of the action of charcoal on $KNO_3$ and of the influence of temperature on the interaction has been undertaken. Evidences from all the experiments show that charcoal acts in two different stages (*i*) $4KNO_3+2C \longrightarrow 4KNO_2+2CO_2$ and (*ii*) $4KNO_2+3C \longrightarrow 2K_2CO_3+CO_2+2N_2$ These are followed under suitable conditions by the flash reaction (*iii*) $KNO_3+KNO_2+2C \longrightarrow K_2CO_3+CO_2+N_2$.

Reaction (*ii*) is the major reaction in the interaction and proceeds through the dissociation of the potassium nitrite, produced in (*i*) into potassium oxide, nitric oxide and nitrogen tetroxide. This is followed by a chain of vigorous reactions between the nitric oxide and nitrogen tetroxide with charcoal, and the fixation of the carbon dioxide, thus produced, in the $K_2O$ as potassium carbonate. The proportion of $N_2 : CO_2$ in the reaction is 2 : 1.

Depending on conditions, the reaction may proceed smoothly to completion, the reactions (*i*) and (*ii*) going on concurrently producing carbon dioxide and nitrogen in the ratio of 3 : 2, or it may develop speed, become violent and produce a flash In the flash stage, the reaction (*iii*) occurs, potassium nitrite being then produced from the nitrate in two ways . (*a*) by reduction with charcoal as in (*i*) and (*b*) by direct rupture into potassium nitrite and oxygen. The reaction chain, initiated by potassium nitrite, proceeds in full swing and charcoal burns in the mixture of nitric oxide and oxygen producing a flash. The proportion of $N_2 : CO_2$ in the flash reaction is as 1 . 1.

In Part I (Oza and Shah, *J. Univ. Bom.*, 1942, **11**, *iii*, 56) it has been shown that the usual reaction $4KNO_3+5C \longrightarrow 2K_2CO_3+3CO_2+2N_2$, attributed to the action of charcoal on potassium nitrate is, in all probability, made up of at least two consecutive reactions proceeding as

$$4KNO_3+2C \longrightarrow 4KNO_2+2CO_2 \qquad \dots \quad (i)$$

and

$$4KNO_2+3C \longrightarrow 2K_2CO_3+CO_2+2N_2 \qquad \dots \quad (ii)$$

and that the reaction (*ii*) is, probably, the net result of several side or consecutive reactions. It has also been shown there that the interaction with 20% charcoal at 390° steadily develops speed and the reaction (*i*) becomes violent and then culminates into a flash if KOH is included in the system, the reaction (*ii*) then slackens without the production of flash if both the carbon dioxide and nitrogen are pumped off continuously as they are formed.

With a view to elucidating the factors controlling the flash the effect of (*a*) mass of charcoal and (*b*) temperature, on the interaction is studied in detail and to substantiating the evidence obtained, the interaction between charcoal and (*i*) potassium nitrite and (*ii*) mixtures of potassium nitrite and potassium nitrate of known composition is also investigated. The results of these investigations are set out in this paper.

## EXPERIMENTAL

The materials used, the apparatus and the mode of work were exactly the same as those described in Part I (*loc. cit.*).

### *The Effect of Mass of Charcoal*

The occurrence of flash in the interaction between potassium nitrate and 20% charcoal when KOH is included in the system and its absence when the evolved gas is all pumped off led to examination of the effect of more than 20% charcoal under the two conditions.

Experiments with 25 and 30% charcoal showed that flash occurred in all the experiments under both the conditions. The results are given in Table I.

TABLE I

*Flash expts. at 390° with 0·4g. $KNO_3$ and 25 and 30% charcoal with and without KOH in the system*

(*a*) without KOH

| C. | T in min. | Gas evolved (composition in c c.). | | | | | | Gas evolved (% compositin). | | | | | Ratio. | Residue (g.) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Total. | $N_2$. | $CO_2$. | NO. | CO | $N_2O_3$ | $N_2$ | $CO_2$. | NO. | CO | $N_2O_3$ | $N_2.CO_2$ | $K_2CO_3$ | $KNO_2$ | $KNO_3$. |
| 25% | 4 | 96·7 | 37·6 | 52·8 | 0·4 | 5·9 | — | 38·9 | 54·6 | 0·4 | 6·1 | — | 1:1·4 | 0·231 | 0·0235 | 0·0313 |
| 30 | 4 | 108·1 | 40·8 | 60·9 | 3·1 | 3·7 | — | 37·7 | 56·3 | 2·9 | 3·0 | — | 1:1·5 | 0·258 | 0·0133 | Trifle |

(*b*) with KOH

| C. | T in min. | Total. | $N_2$. | $CO_2$. | NO. | CO | $N_2O_3$ | $N_2$ | $CO_2$. | NO. | CO | $N_2O_3$ | $N_2.CO_2$ | $K_2CO_3$ | $KNO_2$ | $KNO_3$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | 3 | 95·7 | 36·9 | 52·5 | 2·0 | 4·3 | 1·0 | 38·5 | 54·9 | 2·1 | 4·5 | 1·1 | 1:1·4 | 0·218 | 0·0200 | 0·0344 |
| 30 | 3 | 101·4 | 37·3 | 56·3 | 4·5 | 3·3 | 0·7 | 36·5 | 55·5 | 4·4 | 3·3 | 0·7 | 1:1·5 | 0·248 | 0·0124 | 0·0300 |

TABLE II

*Expts. at 390° with 0·5 g. $KNO_3$ and 14, 16, 18, 20 and 22% charcoal to examine the interaction in stages*

| C% | T (min) | Total. | Gas evolved (composition) in c.c | | | | Diff bet. consecutive stages | | Ratio $N_2:CO_2$ from (5) | Gas evolved (% composition). | | | | Residue (g) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $N_2$. | $CO_3$ | NO. | CO | | | | $N_2$ | $CO_2$ | NO | CO. | $K_2CO_3$ | $K_2CO_3$ per cc of $N_2$ | $KNO_2$ in g. | $KNO_2$ (diff. between stages) | $KNO_3$ in g |
| 1 | 2 | 3 | 4 | | | | 5 | | 6 | 7 | | | | 8 | 9 | 10 | 11 | 12 |
| 14 | 8 | 22·8 | 7·9 | 13·8 | 0·1 | 0·5 | 7·9 | 13·8 | 1:1·7 | 35·4 | 61·9 | 0·4 | 2·3 | 0·055 | 0·007 | 0·0034 | — | 0·4218 |
| ,, | 18 | 42·8 | 16·0 | 26·3 | 0·1 | 0·4 | 8·1 | 12·5 | 1:1·5 | 37·4 | 61·4 | 0·2 | 1·0 | 0·110 | 0·0068 | 0·0031 | 0·0000 | 0·3531 |
| ,, | 36 | 64·6 | 24·1 | 39·8 | 0·2 | 0·5 | 8·1 | 13·5 | 1:1·7 | 37·3 | 61·6 | 0·3 | 0·8 | 0·171 | 0·0075 | 0·0066 | 0·0034 | 0·2800 |
| ,, | 75 | 90·8 | 34·4 | 55·3 | 0·7 | 0·4 | 10·3 | 15·5 | 1:1·5 | 37·9 | 60·9 | 0·8 | 0·6 | 0·228 | 0·0056 | 0·0091 | 0·0025 | 0·1815 |
| 16 | — | 32·4 | 12·1 | 19·9 | 0·1 | 0·3 | 12·1 | 19·9 | 1:1·6 | 37·3 | 61·4 | 0·3 | 1·0 | 0·089 | 0·0074 | 0·0044 | — | 0·3814 |
| ,, | — | 55·6 | 21·0 | 34·1 | 0·2 | 0·3 | 8·9 | 14·2 | 1:1·6 | 38·0 | 61·4 | 0·3 | 0·6 | 0·142 | 0·0060 | 0·0143 | 0·01 | 0·2963 |
| ,, | 80 | 79·1 | 26·5 | 51·1 | 0·8 | 0·7 | 5·5 | 17·0 | 1:3·1 | 33·5 | 64·6 | 1·0 | 0·9 | 0·1605 | 0·0034 | 0·0195 | 0·0052 | 0·2390 |
| ,, | 135 | 100·9 | 33·9 | 66·1 | 0·9 | 1·0 | 7·4 | 15·0 | 1:2·0 | 33·6 | 65·5 | 0·9 | 1·0 | 0·2054 | 0·0061 | 0·0270 | 0·0075 | 0·1632 |
| 18 | 5 | 14·2 | 3·0 | 10·3 | 0·5 | 0·4 | 3·0 | 10·3 | 1:3·4 | 26·1 | 70·0 | 3·5 | 2·9 | 0·0160 | 0·0053 | 0·0009 | — | 0·4618 |
| ,, | 18 | 31·0 | 8·1 | 21·8 | 0·5 | 0·4 | 5·1 | 11·5 | 1:2·1 | ,, | 70·0 | 1·5 | 2·0 | 0·0346 | 0·0036 | 0·0012 | 0·0003 | 0·4176 |
| ,, | 45 | 56·3 | 17·6 | 38·3 | 0·4 | 1·0 | 9·5 | 16·5 | 1:1·7 | 30·7 | 66·8 | 0·7 | 1·8 | 0·0970 | 0·0065 | 0·0016 | 0·0004 | 0·3345 |
| ,, | 62 | 83·6 | 26·8 | 54·8 | 1·7 | 1·3 | 9·2 | 16·5 | 1:1·8 | 31·7 | 64·8 | 2·1 | 1·6 | 0·1648 | 0·0074 | 0·0037 | 0·0021 | 0·2500 |
| ,, | 93 | 108·6 | 37·9 | 69·2 | 1·0 | 1·4 | 10·2 | 14·4 | 1:1·4 | 34·2 | 63·7 | 0·9 | 1·3 | 0·2270 | 0·0061 | 0·0056 | 0·0019 | -- |
| 20 | 4 | 19·3 | 2·2 | 15·8 | 0·7 | 0·6 | 2·2 | 15·8 | 1:7·2 | 11·4 | 81·9 | 3·7 | 3·1 | 0·0136 | 0·0062 | 0·0009 | — | 0·4571 |
| ,, | 14 | 36·0 | 7·0 | 27·3 | 0·9 | 0·8 | 4·8 | 11·5 | 1:2·4 | 26·4 | 69·3 | 2·5 | 2·2 | 0·0435 | 0·0062 | 0·0009 | 0·0000 | 0·4172 |
| ,, | 27 | 61·8 | 18·5 | 41·8 | 0·8 | 0·7 | 11·4 | 14·5 | 1:1·3 | 30·0 | 67·8 | 1·3 | 1·1 | 0·1068 | 0·0055 | 0·0022 | 0·0013 | 0·3186 |
| ,, | 70 | 108·5 | 36·3 | 69·5 | 1·1 | 1·6 | 17·8 | 27·7 | 1:1·6 | 33·4 | 64·5 | 1·0 | 1·5 | 0·2130 | 0·0060 | 0·0035 | 0·0013 | 0·1608 |
| 22 | 2·5 | 24·3 | 5·3 | 17·7 | 0·8 | 0·5 | 5·3 | 17·7 | 1:3·3 | 21·8 | 72·8 | 3·3 | 2·0 | 0·0176 | 0·0033 | 0·0146 | — | 0·4256 |
| ,, | 5·0 | 64·3 | 19·1 | 43·4 | 0·8 | 0·5 | 13·8 | 25·7 | 1:1·9 | 30·0 | 67·4 | 1·2 | 1·6 | 0·1008 | 0·0060 | 0·0188 | 0·0042 | 0·2985 |
| ,,<br>Flash | 7·0 | 112·2 | 42·1 | 64·1 | 1·4 | 4·6 | 23·0 | 20·7 | 1:0·9 | 37·5 | 57·1 | 1·2 | 4·1 | 0·2713 | 0·0074 | 0·0230 | 0·0042 | 0·0542 |

The interaction is considerably accelerated by increase in the proportion of charcoal, time required for the production of flash (3 to 4 min.) being much less than that in the experiments with 20% charcoal (about 24 min.) The proportions of the components of both the solid residue and the evolved gas in the two sets of experiments compare favourably with those in the flash experiments with 20% charcoal and with each other.

It is evident that the cause for the occurrence of flash is to be sought for in the composition of the reacting mass more than in any superimposed condition such as inclusion of KOH in the system.

Evidently if the interaction be examined at several intermediate stages between the beginning and end of the reaction with varying proportions of charcoal, the nature and amounts of the reaction products at intermediate stages may be revealed and thus it may throw light on the mechanism of the reactions responsible for the production of flash. Series of experiments were therefore performed with 0·5 g. of potassium nitrate and 14, 16, 18, 20, and 22% charcoal and in each series reactions were allowed to proceed to different extents and the products of the interaction examined as usual. As the flash occurred with 22% charcoal, experiments with higher proportion of charcoal were not deemed essential. The results of this series are given in Table II and graphs of the volumes of nitrogen against amounts of potassium carbonate shown in Fig. 1.

The results show that :

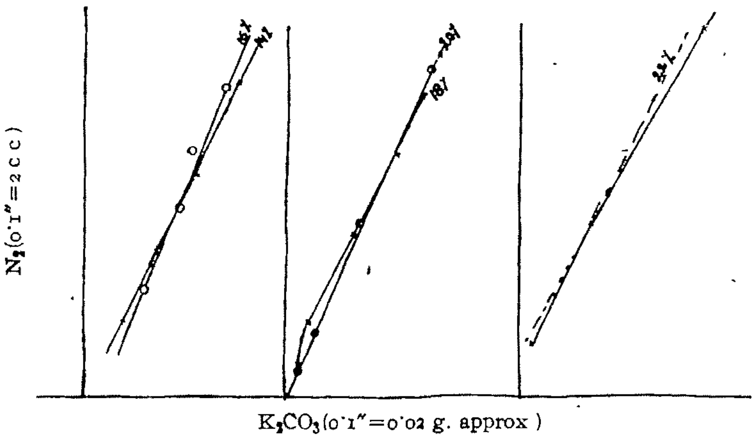
(*i*) The ratio $N_2 . CO_2$ (column 6) is fairly constant, averaging to 1 : 1·6 in all stages with 14% C and fluctuated very much with others. This ratio steadily increases in the initial stage with the amount of charcoal, being as much as 1 : 7·2 with 20% charcoal (the corresponding stage with 22% C is very vigorous). In the flash stage this ratio becomes 1 : 0·9.

(*ii*) The amounts of potassium nitrite (column 10), which show irregularity when end stages are compared in accordance with the previous observations (Part I, Tables I and II), show more or less complete uniformity from stage to stage in any single set of experiments. Its amount is the greatest in the end stage with 16% C, and an amount comparable with it is found only in the flash stage with 22% C. This implies that the charcoal content of the reacting system has much to do with the production of potassium nitrite and also that perhaps a certain optimum concentration of this substance is demanded by the flash reaction and that this probably operates through time factor (column 2). Column 11 shows that there are fluctuations in the amounts of potassium nitrite from stage to stage up to 18% C but after this its amount, at all stages, in any single set, becomes steady Thus with 20% and 22% C, there is a constant difference in the amount of potassium nitrite from stage to stage indicating a constant rate of its formation and decomposition. This rate is far higher in reactions with 22% C than with 20% C.

(*iii*) The amounts of potassium carbonate formed (column 9) increase proportionately with the production of nitrogen in all experiments thus showing that the mass of charcoal influences the production of nitrogen and potassium carbonate in practically the same way. With 22% C the production of potassium carbonate is greater in the flash stage than in the preceding stages ; a similar quantity is formed with 18% C as well. Here, however, the vigour of the reaction, modulated by the charcoal content of the system, is very slow. This would mean that for the same quantity of potassium carbonate there is less nitrogen formed during the flash stage than in the preceding stages.

(*iv*) Nitric oxide and carbon monoxide (column 7) are produced in small amounts. Their amounts are irregular and appear, in general, to depend on the proportion of charcoal used. The amounts of nitric oxide and nitrogen tetroxide are usually higher in the initial stage and in the flash stage than in other stages. The amounts of the oxides of nitrogen found in any stage should depend upon (*a*) pressure under which the experiment is conducted, low pressure raging for a long time tending to draw some of he gases formed and normally undergoing further reaction with charcoal, out of the place of their origin inspite of their great reactivity to charcoal; (*b*) quantity of charcoal then present in the system, an insufficient quantity permitting their escape; and (*c*) the rate with which they are formed at the place of their oirgin, since charcoal, even if present in sufficient amount, may not be able to abruptly reduce a large quantity of the gases suddenly formed. It is likely that the cause (*a*) operates in the initial stages, (*b*) operates in the few isolated stages (*e.g.* in experiments with 18% C, where unusual quantity of potassium carbonate is found to have been formed in absence of flash and (*c*) operates in the flash.

FIG. I



(*v*) Potassium nitrate is present in the residue even after the flash though in small amount.

It was observed that the mercury of the pump was practically unaffected, except at the start in experiments with 14% C and the effect was greater, the greater the percentage of charcoal used and was noticeable in 18% and 22% C.

### *Effect of Temperature*

One of the most important indications of the above series of experiments is that the ratio $N_2 : CO_2$ tends to become unity in the flash stage. With a view to testing this observation a series of experiments was planned to separate the gaseous reaction products of the flash stage from those of the preceding stages. The experiments were conducted with 0·3 g. of potassium nitrate and 20% charcoal. Smaller quantities were used to avoid repeated fractures of the apparatus by the violence of the reaction. The temperatures used were 395°, 400°, 410° and 420°. Higher temperatures were preferred in order to observe at the same time the effect of temperature. The evolved gas was continuously pumped off till the flash occured, when the time was noted and the tap P (Fig 1, p, 57, Part I) was turned off and the gas on the pump side collected along with that already pumped off (A). The tap was next opened and the gaseous products of the flash stage collected separately (B). The gases (A) and (B) and the residue were analysed The results are given in Table III. These show the same general features as before and further that the ratio $N_2 : CO_2$ is, on an average, 1 : 1·7 in (A) and 1 : 1·2 in (B). In view of the facts that (*a*) the rapidity of the reaction near the flash stage does not permit complete separation of the gas (A) from the gas (B) and (*b*) that some potassium nitrite is present in the residue, it would appear reasonable to suppose that in the flash reaction the ratio $N_2 : CO_2$ tends to become 1 : 1.

An attempt was made to examine the reaction at 405° in stages The results are set out in Table IIIA and compare favourably with the results of a similar experiment with 22% charcoal at 390° (Table II) It will be seen in the table that the ratio $N_2$ $CO_2$, referred to differences in their amounts between consecutive stages, is more than 1 : 2·1 in the stages preceding the flash and about 1 :0·9 in the stage attending the flash.

TABLE III

*Flash expts. at higher temps. to separate the gaseous products formed before the flash* (A) *from those formed during the flash* (B).

| Temp | Time for flash to pass | Gas evolved (composition in c c) Total | $N_2$ | $CO_2$ | NO | CO | Ratio. $N_2 : CO_2$ | Gas evolved (% composition) $N_2$. | $CO_2$. | NO | CO. | Residue (g) $K_2CO_3$ | $KNO_2$. | $KNO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 395° | 24 min. | 75·8 | 29·1 | 43·8 | 1·5 | 1·4 | 1 : 1·5 | 38·4 | 57·7 | 1·9 | 1·6 | 0·1945 | 0·0158 | 0·0143 |
| 400 | 13·0 | 72·6 | 28·2 | 41·9 | 1·5 | 1·0 | ,, | 38·8 | 57·7 | 2·0 | 1·3 | 0·1820 | 0·0183 | 0·0169 |
| 410 | 4·5 | 75·0 | 29·3 | 43·3 | 1·5 | 0·9 | ,, | 38·9 | 57·7 | 2·1 | 1·2 | 0·1870 | 0·0143 | 0·0145 |
| 420 | 3·0 | 76·9 | 30·3 | 44·9 | 1·3 | 0·4 | ,, | 39·4 | 58·3 | 1·7 | 0·5 | 0·1905 | 0·0114 | 0·0109 |

| (A) Gas evolved before flash Total gas (c c.) | Composition $N_2$ | $CO_2$. | NO. | CO. | Ratio $N_2 . CO_2$. | % Composition $N_2$. | $CO_2$ | NO | CO. | (B) Gas evolved during flash Total gas (c.c) | Composition. $N_2$ | $CO_2$ | NO. | CO. | Ratio. $N_2 \cdot CO_2$. | % Composition. $N_2$ | $CO_2$. | NO. | CO. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 41·1 | 15·3 | 25·2 | 0·4 | 0·3 | 1 . 1·65 | 37·2 | 61·3 | 1·0 | 0·7 | 34·6 | 13·9 | 18·5 | 1·1 | 1·1 | 1 1·33 | 40·2 | 53·5 | 3·2 | 3·2 |
| 39·3 | 14·7 | 24·2 | 0·2 | 0·3 | ,, | 37·1 | 61·6 | 0·5 | 0·7 | 32·9 | 13·7 | 17·2 | 1·3 | 0·7 | 1 1·25 | 41·7 | 52·3 | 3·9 | 2·1 |
| 43·5 | 16·1 | 27·0 | 0·2 | 0·2 | 1 . 1·7 | 36·9 | 62·4 | 0·5 | 0·5 | 31·3 | 13·4 | 15·7 | 1·3 | 0·7 | 1 1·17 | 42·8 | 50·1 | 4·1 | 2·3 |
| 44·2 | 15·9 | 27·9 | 0·2 | 0·0 | 1 1·75 | 36·1 | 63·2 | 0·5 | 0·0 | 32·5 | 14·4 | 16·5 | 1·0 | 0·4 | 1 1·15 | 44·3 | 50·8 | 3·1 | 1·2 |

TABLE IIIA

*Flash expt. at 405° to examine the interaction in stages with 20% charcoal*

$KNO_3 = 0·4$ g.

| Stage No. | Gas evolved (composition in c c). Total | $N_2$ | $CO_2$ | NO | CO | $N_2O_3$ | Ratio $N_2 \cdot CO_2$ | Gas evolved (%) $N_2$ | $CO_2$ | NO | CO | $N_2O_3$ | Residue (g.). $K_2CO_3$. | $KNO_2$ | $KNO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 36·8 | 11·3 | 24·0 | 0·1 | 0·5 | 0·9 | 1 . 2·1 | 30·7 | 65·2 | 0·3 | 1·4 | 2·5 | 0·0707 | 0·0180 | 0·2700 |
| 2 | 48·2 | 14·8 | 31·8 | 0·0 | 0·6 | 1·0 | 1 : 2·1 | 30·7 | 65·9 | 0·0 | 1·3 | 2·0 | 0·1025 | 0·0185 | 0·2367 |
| 3 Flash | 94·6 | 37·6 | 52·5 | 2·5 | 1·3 | 0·8 | 1 . 1·4 | 39·8 | 55·5 | 2·6 | 1·5 | 0·8 | 0·2367 | 0·0267 | 0·0223 |

The observations in Table II have also shown that there is a rapid rate of formation and consumption of potassium nitrite under conditions conducive to the production of flash ; and that potassium nitrate is present in the residue after the flash. From these it would appear that both potassium nitrate and potassium nitrite may take part in the reaction producing the flash. This together with the facts that the ratio $N_2 : CO_2$ approximates to 1 : 1·5 in all experiments wherein the reaction proceeds to end, becomes 1 :7·2 in the initial stage with 20% charcoal and tends to be 1 : 1 in the flash stage of the reaction, confirm the observation recorded in Part I regarding the composite nature of the reaction : $4KNO_3 + 5C \rightarrow 2K_2CO_3 + 3CO_2 + 2N_2$, and indicates that in the flash reaction equivalent quantities of the nitrite and the nitrate may be reacting with charcoal to produce carbon dioxide and nitrogen in the ratio 1 : 1.

### *The Action of Charcoal on (i) Potassium Nitrite and (ii) Mixtures of Potassium Nitrite and Potassium Nitrate*

Since oxides of nitrogen are present in all experiments it would seem that a study of (*i*) the thermal decomposition of potassium nitrate and (*ii*) the action of charcoal on (*a*) potassium nitrite and (*b*) known mixtures of potassium nitrite and potassium nitrate may provide important information on the course of the reactions under investigation. The thermal decomposition of potassium nitrite (Oza and Shah, *J. Univ. Bom.*, 1942, **11**, *iii*, 70) was studied in this connection. The results showed that potassium nitrite dissociates at its melting point (about 419°) into potassium oxide, nitric oxide and nitrogen tetroxide according to the equation :

$$2KNO_2 = K_2O + NO + NO_2 \qquad \ldots \quad (1)$$

and the nitrogen tetroxide formed acts upon the undecomposed potassium nitrite to produce nitrogen or/and nitric oxide as : $2KNO_2 + NO_2 \rightarrow 2KNO_3 + N$ (2) and $KNO_2 + NO_2 \rightarrow KNO_3 + NO$ (3). The potassium nitrate formed in (2) and (3) undergoes scission into potassium nitrite and oxygen under the experimental conditions, the process being aided by the nitric oxide present in the system which removes oxygen from the system as nitrogen tetroxide, the latter influencing the reactions (1), (2) and (3).

An investigation on the effect of charcoal on potassium nitrite showed that the reaction starts in the vicinity of 390°, the exact temperature depending slightly on the proportion of charcoal used. The reaction is always violent* becoming so within a few seconds of its start and then comes to a stop, the violence being accompanied by scintillation of charcoal particles but no flash. The violence of the reaction is very great and the apparatus often cracked even with only 0·2 g. of potassium nitrite.

An examination of the gaseous products and the solid residue showed the presence of (*i*) nitrogen†, carbon dioxide, nitric oxide, nitrogen tetroxide and carbon monoxide, and (*ii*) potassium carbonate, potassium nitrite and potassium nitrate. Potassium oxide, azide, cyanate and hyponitrite were tested for and found to be absent. The apparatus and the method of experimentation were the same as before. After evacuating the apparatus the column was surrounded by the electric furnace maintained at 350° and the temperature gradually raised. Not the slightest evolution of any gas was observed till the temperature at which the reaction became violent was reached. Near this temperature a few bubbles of gas were soon followed by a sudden release of a large volume of gas. The temperature was noted. The results of these experiments are given in Table IV and the potassium carbonates formed plotted against the evolved nitrogen in Fig. 2.

The results show that (*i*) total quantity of the evolved gas increases with the increase in the percentage of charcoal ; (*ii*) there is a steady change in the composition of the evolved gas as the proportion of charcoal used increases : the ratio $N_2 . CO_2$ passes steadily from 1:0·4 with 5% charcoal to 1.0 8 with 100%,‡ the average value of the ratio being 1:0·5 ; (*iii*) potassium nitrite is always present in the residue and also potassium nitrate. The amount of potassium nitrite consumed in an experiment is proportional to that used in the experiment, while the amounts of potassium nitrate formed are small being appreciable only in the slow experiment with 5% charcoal ; (*iv*) the linear relationship between the quantities of potassium carbonate and nitrogen formed is evident from the figure.

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* The vigour of the reaction could be slackened only by very cautious regulation of temperature if the proportion of charcoal is reduced to 5%.

† A small quantity of nitrous oxide was detected in the slow reaction experiment with 5 % charcoal

‡ Percentage of charcoal refers always to the mass of nitrate or nitrite or mixture of the nitrate and nitrite used.

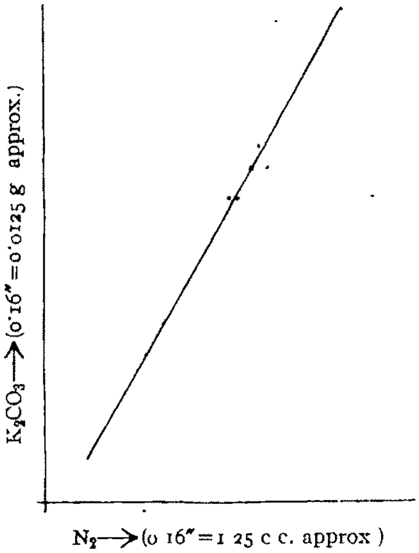
TABLE IV

*Decomposition of* $KNO_2$ *in presence of different amounts of charcoal*

| C%. | $KNO_2$ taken g | Temp. of reaction. | Gas evolved in c.c. at N T P. | | | | | Gas evolved in %. | | | | Residue (g ). | | | Ratio $N_2:CO_2$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total | $N_2$ | $C_2$ | NO | CO. | $N_2$ | $CO_2$ | NO | CO. | $K_2CO_3$. | $KNO_3$. | $KNO_2$ | |
| 5* | 0·1129 | 412-13° | 8·9 | 5·9† | 2·3 | 0·6 | 0·1 | 66·1 | 25·9 | 7·0 | 1·0 | 0·0423 | 0·0264 | 0·0344 | 1 :0·4 |
| 10 | 0·1405 | 406-07 | 19·2 | 12·5 | 5·1 | 1·4 | 0·2 | 65·0 | 26·6 | 7·2 | 1·2 | 0·0774 | 0·0011 | 0·0498 | ,, |
| 15 | 0·1255 | 403-04 | 20·1 | 12·9 | 5·4 | 1·5 | 0·3 | 64·3 | 27·0 | 7·5 | 1·2 | 0·0874 | 0·0022 | 0·0214 | , |
| 20 | 0·1242 | 401-02 | 22·9 | 14·5 | 6·3 | 1·8 | 0·3 | 63·4 | 27·6 | 7·7 | 1·3 | 0·0901 | 0·0019 | 0·0142 | ,, |
| 25 | 0·1884 | 398-9 | 33·0 | 20·3 | 9·3 | 2·6 | 0·8 | 61·5 | 28·2 | 7·9 | 2·4 | 0·1249 | 0·0024 | 0·0330 | 1 :0·45 |
| 50 | 0·1216 | 391-2 | 25·1 | 13·8 | 7·8 | 2·2 | 1·3 | 55·2 | 31·7 | 8·6 | 4·5 | 0·0943 | — | 0·0139 | 1 :0·56 |
| 100‡ | 0·1153 | 385-6 | 26·2 | 12·5 | 9·6 | 2·6 | 1·8 | 47·6 | 36·6 | 10·0 | 6·8 | 0·0820 | — | 0·0135 | 1 :0·77 |

It is both interesting and important to notice that it is the average value of the ratio $N_2:CO_2$ which is 1:0·5, and not the actual value, in any single experiment. The latter depends on the proportion of charcoal used. This indicates that the reaction is complex. In view of the fact that nitric oxide and nitrogen tetroxide are invariably present in the gasous reaction products it would seem likely that these form the intermediate products in the reaction culminating in the formation of potassium carbonate, carbon dioxide and nitrogen. Such a view is consistent with what is known about the thermal decomposition of potassium nitrite (*loc. cit.*) and about the behaviour of nitric oxide (Shah, *J. Chem. Soc.*, 1929, 2661) and of nitrogen tetroxide (Trivedi, Bombay University M.Sc. thesis, 1941) to charcoal.

FIG. 2



The results of the action of charcoal on known mixtures of potassium nitrate and potassium nitrite are given in Table V.

The results show that (*i*) in all experiments the interaction becomes violent ; the violence is accompanied with flash up to 25% potassium nitrite and of scintillation but *no flash* in experiments with 100%. No flash was actually noticed in the 50% experiment ; (*iii*) the time needed for the violent reaction to occur is less, the greater the quantity of potassium nitrite used and *whenever a flash is produced there is always a definite time lag before it is observed*; (*iv*) with the increase in the percentage of potassium nitrite there is an increase in the production of potassium carbonate and nitrogen and a decrease in the production of carbon dioxide ; (*v*) both potassium nitrite and potassium nitrate are present in the residue and some nitric oxide, nitrogen tetroxide and carbon monoxide are always present in the gaseous products.

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* In this experiment alone the reaction could be controlled Heating continued cautiously for 15 min

† Some nitrous oxide was detected in the nitrogen here.

‡ KOH was included in the apparatus in this experiment, the $N_2O_3$ formed there was 0·33 c c.

TABLE V

*Expts. at 405° with known mixtures of* $KNO_3$ *and* $KNO_2$ *with 2% charcoal.*
Wt. of the mixture = 0·2 g.

| $KNO_2$. | $KNO_3$ | Reaction violent within. | Composition of gas evolved in c c. (N.T.P ) | | | | | Gas evolved (%). | | | | Residue (g.) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total. | $N_2$. | $CO_2$. | NO. | CO. | $N_2$. | $CO_2$ | NO. | CO. | $K_2CO_3$ | $KNO_2$. | $KNO_3$. |
| 0·0% | 100·0% | 7-8 min. | 46·8 | 16·8 | 26·5 | 2·2 | 1·4 | 35·9 | 56·6 | 4·7 | 3·0 | 0·1186 | 0·0138 | 0·0021 |
| 6·25 | 93·75 | 6-7 | 46·4 | 17·4 | 26·3 | 1·6 | 1·2 | 37·2 | 56·6 | 3·4 | 2·6 | 0·1152 | 0·0106 | 0·021 |
| 12·50 | 87·50 | 5-6 | 49·8 | 20·0 | 27·5 | 1·5 | 0·8 | 40·2 | 55·2 | 3·0 | 1·6 | 0·1211 | 0·0106 | 0·0118 |
| 25·00 | 75·00 | 4-5 | 44·1 | 18·5 | 23·4 | 1·4 | 0·7 | 41·9 | 53·5 | 3·2 | 1·6 | 0·1263 | 0·0106 | 0·0177 |
| 50·0 | 50·0 | 0-1 | 40·2 | 20·3 | 18·0 | 1·4 | 0·6 | 50·5 | 44·8 | 3·5 | 1·6 | 0·1250 | 0·0117 | 0·0024 |
| 100·0 | 0·0 | Immediate | 32·1 | 23·4 | 8·8 | 2·5 | 0·4 | 63·4 | 27·5 | 7·7 | 1·4 | 0·1277 | 0·0414 | 0·003 |

KOH solution included in the apparatus in the last expt gave 0·55 c c of $N_2O_3$

## DISCUSSION

The observations recorded in Parts I and II throw light on the mechanism of the action of charcoal on potassium nitrate. Potassium nitrate (m.p. 335°), decomposing into nitrite and oxygen only on strong heating, becomes reduced to the nitrite in presence of charcoal at 250°. The fact that the mass of charcoal accelerates the interaction whereas the mass of potassium nitrate has no similar effect shows that the surface of charcoal plays an important part in the interaction. Further, the fact that no oxygen or carbon dioxide is evolved at 250° and the residue still shows the presence of nitrite indicates that oxygen of the nitrate is retained by charcoal in some state (Rhead and Wheeler, *J. Chem. Soc.*, 1913, **103**, 461 ; Keyes and Marshall, *J. Amer. Chem. Soc.*, 1927, **49**, 158 ; Shah, *loc. cit.*) on its surface. Again the production of carbon dioxide in the greatest quantity in the commencing stage shows that the retained oxygen is given off at a suitable temperature as,

$$4KNO_3 + 2C \longrightarrow 4KNO_2 + 2CO_2 \qquad \dots \quad (i)$$

The facts that the quantities of potassium nitrite present in the residue are never great and nitrogen and potassium carbonate are always produced along with carbon dioxide show that the the action of charcoal on potassium nitrite, leading to the formation of nitrogen and potassium carbonate, constitutes the second concommitant stage in the interaction. The observation that in some stages in the interaction the amount of nitrogen formed is greater even than that of carbon dioxide, taken together with the fact that the average value of the ratio $N_2$:$CO_2$ in the interaction between potassium nitrite and charcoal is 1:0·5 makes it highly probable that the second stage of the interaction is

$$4KNO_2 + 3C \longrightarrow 2K_2CO_3 + CO_2 + 2N_2 \qquad \dots \quad (ii)$$

The absence of potassium oxide and the production of potassium carbonate and nitrogen in linear proportions with respect to each other suggest that the reaction (*ii*) is a simple one. But the facts that in the interaction between potassium nitrite and charcoal (*a*) the actual composition of the products depends on the relative proportions of the reactants, (*b*) the interaction, once started becomes almost necessarily violent giving out scintillations of charcoal particles, (*c*) nitric oxide and nitrogen tetroxide are always present in the gaseous reaction products and (*d*) some potassium nitrate is always present in the residue show beyond doubt, that the reaction is dependent on the reactions involved in the thermal decomposition of potassium nitrite:

$$2KNO_2 \rightleftharpoons K_2O + NO + NO_2 \qquad \ldots \quad (iii)$$

$$4KNO_2 + 2NO_2 \rightarrow 4KNO_3 + N_2 \qquad \ldots \quad (iv)$$

$$KNO_2 + NO_2 \rightarrow KNO_3 + NO \qquad \ldots \quad (v)$$

with the difference that, in the present case, the extent of the reactions (*iv*) and (*v*) is very limited as the nitrogen tetroxide and nitric oxide (Shah, *loc. cit.*) react readily and completely with charcoal,* as

$$2C + 2NO_2 \rightarrow 2CO_2 + N_2 \qquad \ldots \quad (vi)$$

$$C + 2NO \rightarrow CO_2 + N_2 \qquad \ldots \quad (vii)$$

so that the balanced reaction (*iii*) proceeds from left to right. The removal of potassium oxide as

$$K_2O + CO_2 \rightarrow K_2CO_3 \qquad \ldots \quad (viii)$$

accelerates it. Thus, the presence of charcoal induces a chain of vigorous reactions by its action on nitric oxide and nitrogen tetroxide. The reaction (*ii*) may therefore be represented, severally and compositely as

$$\begin{array}{lr}
2(2KNO_2 \rightleftharpoons K_2O + NO + NO_2) & \ldots \quad (iii) \\
2C + 2NO_2 \rightarrow 2CO_2 + N_2 & \ldots \quad (vi) \\
C + 2NO \rightarrow CO_2 + N_2 & \ldots \quad (vii) \\
2K_2O + 2CO_2 \rightarrow 2K_2CO_3 & \ldots \quad (viii) \\
\hline
4KNO_2 + 3C \rightarrow 2K_2CO_3 + CO_2 + 2N_2 & \ldots \quad (ii)
\end{array}$$

The presence of carbon monoxide in the gases is due to the tendency of the sorbed oxygen in charcoal to come off in this form as the charcoal particles scintillate during their rapid interaction with oxides of nitrogen.

The interaction between potassium nitrite and charcoal constitutes a major stage in the reaction under study. It is this stage which decides whether the reaction shall be smooth or violent. At a low temperature and with a low percentage of charcoal the reaction is slow. With rise in temperature and increase in the percentage of charcoal it gains speed and above the optimum temperature and percentage of charcoal, it becomes violent and produces a flash. Both the interactions : $KNO_2 + C$ and $KNO_3 + C$, become violent at about the same temperature and in both the reactions the products are almost exactly similar. The important difference between the two violent reactions is that while the latter becomes so only after a definite time lag and is accompanied with a flash, the former is violent with start and is never accompanied with flash but only scintillation of charcoal particles. Before the flash is produced the $KNO_3 + C$ reaction gains great speed in which potassium nitrite is produced and used up at a constant high rate. In view of the facts that (i) potassium nitrate is always present at the beginning and the end of the flash reaction and (ii) the violent reaction between potassium nitrite and charcoal is never accompanied with flash it appears likely that both potassium nitrite and potassium nitrate take part in the production of flash. This and the fact that the proportion of $N_2:CO_2$ in the flash stage tends to become 1 : 1, make it highly probable that the reaction in the flash stage may be

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* These reactions, supposed to proceed through sorbed oxygen, are represented in this way only for the sake of convenience.

$$KNO_3 + KNO_2 + 2C \rightarrow K_2CO_3 + CO_2 + N_2 \qquad \ldots \quad (ix)$$

Direct experimentation with 50% of the nitrite and the nitrate shows that the reaction is instantaneous, as expected, produces nitrogen and carbon dioxide in the ratio of 1 : 1, also as expected, and is, in general, similar to the flash reaction but *does not produce any flash.* The flash is seen in all experiments up to 25% potassium nitrite in all of which violence sets in less than a minute. The cause of the flash lies, evidently, in something circumstantial. The only conceivable difference between the two reactions, which we may call the natural and the artificial, may be in the temperature condition of the reacting mass Since the involved reactions are all exothermic, the local temperature of the reacting mass in the natural mixture may be higher than that in the artificial one and at the high temperature prevailing in the natural mixture, some of the potassium nitrate might undergo scission into potassium nitrite and oxygen ; the nitrogen tetroxide from potassium nitrite might also produce oxygen under the equilibrium condition $2NO_2 \rightleftharpoons 2NO + O_2$, so that the flash stage in the interaction might correspond to the combustion of charcoal in oxygen and nitric oxide as

$$2C + 2NO + O_2 \rightarrow 2CO_2 + N_2{}^{*} \qquad \ldots \quad (x)$$

Thus, on the whole, the flash reaction may, severally and compositely, be thus represented:

$$\begin{array}{cr}
2KNO_3 \rightarrow 2KNO_2 + O_2 & \ldots \quad (xi) \\
2(2KNO_2 \rightleftharpoons K_2O + NO + NO_2) & \ldots \quad (iii) \\
2NO_2 \rightleftharpoons 2NO + O_2 & \ldots \quad (xii) \\
2(2C + 2NO + O_2 \rightarrow 2CO_2 + N_2) & \ldots \quad (xiii) \\
2(K_2O + CO_2 \rightarrow K_2CO_3) & \ldots \quad (viii) \\
\hline
2(KNO_3 + KNO_2 + 2C \rightarrow K_2CO_3 + CO_2 + N_2) & \ldots \quad (ix)
\end{array}$$

The observations that the flash is accompanied with the production of larger amounts of nitric oxide, nitrogen tetroxide and carbon monoxide and that the production of flash is accelerated by increase in the proportion of charcoal and by a rise in temperatute are in accord with this view.

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* This might involve intermediate formation and oxidation of carbon monoxide as

$$\begin{array}{c}
4C + 2NO + O_2 \rightarrow 4CO + N_2 \\
4CO + 2NO + O_2 \rightarrow 4CO_2 + N_2 \\
\hline
2(2C + 2NO + O_2 \rightarrow 2CO_2 + N_2),
\end{array}$$

# DERIVATION OF TROUTON'S RULE

By M. S. Telang

Various methods of deriving Trouton's rule are reviewed and a new method of derivation is proposed.

Trouton (*Phil. Mag.*, 1884, *v*, **18**, 54) pointed out an interesting and important relation between the latent heat of vaporisation ($l$) of a substance and its absolute boiling point ($T_B$) under a pressure of one atmosphere and this has come to be known as Trouton's rule.

$$\frac{Ml}{T_B} = \frac{\Delta H}{T_B} = \text{constant} \qquad \dots \quad (1)$$

where $M$ is the molecular weight. This relation may also be considered as expressing the constancy of the entropy of vaporisation under the conditions mentioned. However, this rule is only approximately true and when applied to liquids with a wide range of boiling points, the constant shows a distinct deviation. Yet, this empirical rule is an approximation of considerable usefulness when approximate data are needed

Many modifications of Trouton's rule have been proposed from time to time. Each of these modifications brings only some types of compounds into better agreement than what is obtained with the original Trouton's rule. The one that deserves greatest consideration is that due to Hildebrand (*J. Amer. Chem. Soc.*, 1915, **37**, 970).

### *A Review of the Methods of Derivation of Trouton's Rule*

(*i*) By integrating the Clausius-Clapeyron equation, we have

$$\ln p = -\frac{\Delta H}{RT} + I \qquad \dots \quad (2)$$

neglecting the change in $\Delta H$. This equation leads to Trouton's rule for the relation between the heat of vaporisation and the boiling point when $p = 1$ atmos., the value of $I$ for a majority of liquids being nearly 11, which gives

$$\frac{\Delta H}{T_B} = 22$$

at the boiling point (Rodebush and Webb, "Taylor's Treatise on Physical Chemistry", MacMillan & Co., London, 1931, p. 1385).

(*ii*) Cederberg (*Z. physikal. Chem.*, 1911, **77**, 498) derived an equation for calculating Trouton coefficients from critical constants. Thus

$$\frac{\Delta H}{T_B} = \frac{R \ln p_c \, (1 - 1/p_c)}{1 - \dfrac{T_B}{T_c}} \qquad \dots \quad (3)$$

where the critical pressure ($p_c$) is expressed in atmospheres (*cf.* Taylor "Treatise on Physical Chemistry", p. 299). Guldberg (*Z. physikal. Chem.*, 1890, **5**, 374) has indicated that for a large number of normal substances, the absolute boiling point is approximately 0·66 of the critical temperature. Hence, for normal substances, the variation of Trouton's constant is expected to be due to the corresponding variations of $p_c$. However, the values of Trouton's coefficients calculated according to this equation are in fair agreement with the experimental values.

(*iii*) The following equation represents the relation between the relative change in the concentration of the saturated vapour and the energy of vaporisation ($\Delta E$) *i. e.* internal latent heat of vaporisation (Brönsted, "Physical Chemistry", William Heinemann, London, 1937, p. 52).

$$\Delta H - RT = RT^2 \frac{d\,ln\,C}{dT} \text{ or } \Delta E = RT^2 \frac{d\,ln\,C}{dT} \quad \ldots \quad (4)$$

From the kinetic theory, it can easily be shown that during the transition from liquid to vapour (*idem, ibid*, p. 82),

$$\frac{N_1}{N_G} = e^{E_{CR}/kT} \quad \ldots \quad (5)$$

where $N_G$ and $N_1$ represent the number of molecules per c.c. in the vapour and liquid respectively, $E_{CR}$, is the critical energy which liquid molecules must possess in order to penetrate the surface of the liquid and $k$ is the Boltzmann constant. Further,

$$\frac{N_1}{N_G} = \frac{V_G}{V_1}$$

where $V_G$ and $V_1$ are the molar volumes of the vapour and liquid respectively. If these volumes are corrected for the volume occupied by the molecules themselves, then

$$\frac{N_1}{N_G} = \frac{V_G - b}{V_1 - b} = e^{E_{CR}/kT} \quad \ldots \quad (6)$$

where $b$ is the Van der Waals' constant. This equation (6) gives better agreement with experimental values. By differentiating the above equation with respect to temperature,

$$E_{CR} = kT^2 \frac{d\,ln\,N_G}{dT} = \frac{R}{N} T^2 \frac{d\,ln\,N_G}{dT} \quad \ldots \quad (7)$$

This equation is identical with the thermodynamic vaporisation equation (4), if $\Delta E$ is put equal to $NE_{CR}$, where $N$ is the Avogadro number. It follows, therefore, that the heat of vaporisation should be identified with the increase of potential energy which the molecules undergo when they pass from the liquid to the vapour through the surface field of force. Equation (5) predicts that the ratio between the concentrations of molecules in the vapour and in the liquid should be depending only on $E_{CR}/T$, which Trouton discovered from his experimental observations only.

Equation (6) may be written as

$$\Delta E = \Delta H - RT = RT\,ln \frac{V_G - b}{V_1 - b} = RT\,ln \frac{N_1}{N_G}$$

$$\text{or} \quad \frac{\Delta H}{T} = R\left(1 + ln \frac{N_1}{N_G}\right)$$

Hence at the boiling point,

$$\frac{\Delta H}{T_B} = R\left(1 + ln \frac{N_1}{N_G}\right) \quad \ldots \quad (8)$$

This relation (8) has also been deduced from partition functions of liquids (*vide* Butler, *Chem. Soc. Ann. Report*, 1937, **34**, 78, *et. seq.*). By employing the partition function of Fowler and Darwin, for a perfect gas, this function is

$$f_G = (2\pi mkT)^{\frac{3}{2}}\ Vb(T)/Nh^3 \qquad \text{.. (9)}$$

where $b(T)$ is that part of the whole partition function which is dependent upon the vibrational and rotational energy of the molecule. Further, on the assumption that the vibrational and rotational states are the same in the liquid as in the gas, Eyring *et al.* (*Trans Faraday Soc.*, 1937, **33**, 73; *J. Phys. Chem.*, 1937, **41**, 249) give the following expression for the partition function of a liquid

$$f_l = V_F\ \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\ b(T)\ \text{exp.}\ (\Delta E/RT) \qquad \text{... (10)}$$

where $V/N$ is equal to $V_F$, the *free volume* of the liquid. Correlating (9) and (10), and taking logarithms

$$\frac{\Delta E}{T} = R\ ln\ \frac{V_G}{V_F}.$$

Hence, the entropy of vaporization of a liquid is

$$\Delta = S\frac{\Delta H}{T_B} = \frac{\Delta E}{T_B} + R = R\left(1 + ln\ \frac{V_G}{V}\right) \qquad \text{... (11)}$$

which is the same as (8). From Trouton's rule, it is already known that $\Delta H/T_B$ is constant for normal liquids at their boiling points. Hildebrand (*loc. cit.*) showed that a better constancy was found when liquids were compared at temperatures at which they give rise to equal vapour concentrations. Under such conditions, $V_G$ is constant and hence from equation (11) it follows that the free space in the liquid is also constant. It has been indicated by Eyring (*J. Chem. Phys.*, 1936, **4**, 283) that, since the energy required to make a hole in a liquid is the same as that needed to remove a molecule from the liquid, the concentration of holes in the liquid must be evidently equal to the concentration of molecules in the vapour. At equal vapour concentrations, liquids will therefore have equal "concentrations of holes"; in combination with (11) this leads to a simple interpretation of Trouton's rule. When the molecular rotations are not fully developed in the liquid, as in the case of associated liquids in which directed bonds occur, the entropy of vaporisation will be greater than in (11), which is already known from experimental observations.

### *Proposed Method of Derivation of Trouton's Rule.*

Sugden (*J. Chem. Soc.*, 1927, 1781) has given a relation between density and temperature as

$$D - d = D_0(1 - T_R)^{\frac{3}{10}} \qquad \text{... (12)}$$

where $D$ and $d$ are the densities of liquid and vapour respectively, $D_0$ is the density of the supercooled liquid at absolute zero and $T_R$ is the reduced temperature. Neglecting $d$, which is usually small at the boiling point, equation (12) may be written as

$$D = D_0(1 - T_R)^{\frac{3}{10}}.$$

$$\text{Hence}\ \frac{M}{D} = \frac{M}{D_0(1 - T_R)^{\frac{3}{10}}}$$

where $M$ is the molecular weight. So, we have

$$V_0 = V(1 - T_R)^{\frac{3}{10}} \qquad \ldots \quad (13)$$

$V_0$ and $V$ are the zero volume and molecular volume respectively. Further, $0{\cdot}27\ V_c = V_0$ (*Idem*, *ibid.*, 1784), where $V_c$ is the critical volume. Substituting in (13), we get

$$0{\cdot}27\ V_c = V(1 - T_R)^{\frac{3}{10}}.$$

At the boiling point, $T_R = 0{\cdot}66$ (Guldberg, *loc. cit.*); hence one obtains

$$0{\cdot}27\ V_c = V\,(1 - 0{\cdot}66)^{\frac{3}{10}} \text{ or } V_c = 2{\cdot}68\ V \qquad \ldots \quad (14)$$

The thermodynamic equation of state is written as

$$p + \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V \qquad \ldots \quad (15)$$

the quantity $(\partial E/\partial V)_T$ being called the internal pressure (*vide* Brönsted, *loc. cit.*, p. 34)-

If van der Waals equation of state

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \ldots \quad (16)$$

is differentiated at constant volume, we get

$$\left(\frac{dp}{dT}\right)_V = \frac{R}{V - b}.$$

By combining with equation (16), we have

$$p + \frac{a}{V^2} = T\left(\frac{dp}{dT}\right)_V. \qquad \ldots \quad (17)$$

Hence, $$\frac{a}{V^2} = \left(\frac{\partial E}{\partial V}\right)_T$$

(internal pressure) (*cf.* equations 15 & 17).

It follows from (16) that

$$\frac{a}{V^2} = \frac{RT}{V - b} - p = \frac{RT}{V - b}$$

neglecting the external pressure at the boiling point $p = 1$ atmos. in comparison with the internal pressure which is very large. Thus

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{RT}{V - b}.$$

It is known that the internal pressure (Hildebrand, "Solubility", Amer. Chem. Soc. Monograph Series, No. 17, 1936, p. 98, *et seq.*) is given over a limited range of temperature by the expression $\Delta E/V$. Thus we have at the boiling point,

$$\frac{\Delta E}{V}=\frac{RT_B}{V-b} \quad \ldots \quad (18)$$

Since the value of van der Waals' constant $b=V_0/3$, (18) can be written as

$$\frac{\Delta E}{V}=\frac{RT_B}{V-V_0/3}=\frac{RT_B}{(3V-V_0)/3}.$$

Substituting for $V_0$ according to (14), we have

$$\frac{\Delta E}{V}=\frac{3RT_B}{3V-2{\cdot}68V}=18{\cdot}75\ T_B/V,$$

when $R$ is taken as 2 calories, or $\dfrac{\Delta E}{T_B}=18{\cdot}75$ calories/degree ... (19)

Since $\Delta H-RT_B=\Delta E$, we obtain $\dfrac{\Delta E}{T_B}=\dfrac{\Delta H}{T_B}-R=18{\cdot}75$ calories/degree.

$$\text{or} \quad \frac{\Delta H}{T_B}=18{\cdot}75+2=20{\cdot}75 \text{ calories/degree.}$$

So, finally, the entropy of vaporisation is approximately given by the expression

$$\Delta S=\frac{\Delta H}{T_B}=21 \text{ calories/degree.}$$

It may be pointed out that while deriving Trouton's rule by this method, only two empirical relations have been used, *viz.* Guldberg's rule (*loc. cit.*) and the ratio of

$$\frac{V_0}{V_C}=0{\cdot}27 \text{ (Sugden, \textit{loc. cit.})}$$

Sugden's relation between density and temperature (12) is no longer considered as quite empirical since Macleod's equation (*Trans. Faraday Soc.*, 1923, **19**, 38) on which it was based has been derived by Fowler (*Proc. Roy. Soc*, 1937, **A**, **159**, 227; *cf.* Butler, *loc. cit.*, p. 84).

## CONCLUSION

In very polar liquids such as water, alcohols, ammonia and other substances, there is a strong dipole attraction between molecules which would require an extra amount of energy for separation of the molecules into the vapour phase and hence these substances may not be expected to follow this rule. Further, a liquid that is not greatly expanded over its closely packed structure, such as mercury at ordinary temperature, hydrogen and helium which boil only a little above absolute zero, are in a region where repulsive forces have an important part in balancing the attractive forces. It appears from the relation between internal pressure and molal volume (Hildebrand, *loc. cit.*) that elementary substances having a molal volume less than about 60 would not be anticipated to obey this rule.

Furthermore, as shown in (3), the values of Trouton's coefficients are dependent on the critical pressures which in turn are directly related to the internal pressures of liquids at their boiling points (Telang, unpublished work). From this and other foregoing considerations, it is tentatively proposed pending further work, that Trouton's coefficients should be compared not at equal vapour pressure *i.e* the boiling points, but at temperatures at which substances have equal internal pressures.

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# SUCCINIC ACID DEHYDROGENASE FROM CUCUMBER SEEEDS

By K. P. Basu and J. N. Karkun

The preparation and properties of succinic acid dehydrogenase from cucumber seeds are described. Methylene blue cannot serve as hydrogen acceptor, but the enzyme is a perfect dehydrogenase as it can use a dye of higher $p_H$ (2.6-dichlorophenolindophenol blue) as hydrogen acceptor Narcotics inhibit the dehydrogenating property of the enzyme whereas potassium cyanide inhibits the power of utilising oxygen as hydrogen acceptor. Sodium fluoride inhibits the dehydrogenating factor considerably and the oxidase factor feebly Pyrophosphate is inhibitory to both. Incubation for a certain interval with copper sulphate at a concentration, which is usually harmless to the enzyme, greatly inhibits the enzymic activity showing that the enzyme contains a -SH group in the protein molecule

Succinic dehydrogenase is the most widely studied enzyme. Ever since its discovery by Thunberg (*Zentr. Physiol.*, 1916, **31**, 91) from washed muscle it has drawn a good number of workers to this field. The work of Widmark (*Skand. Arch. Physiol.*, 1921, **41**, 200), Ohlosson, *ibid.*; 1921 **41**, 77), Anderson (*ibid.*, 1928, **52**, 187), Alwall (*ibid.*, 1928, **54**, 1), Lohmann (*ibid.*, 1930, **58**, 45), Sen (*Biochem. J.*, 1931, **25**, 849), Borsook and Schott (*J. Biol. Chem.*, 1931, **92**, 535), Ogston and Green (*Biochem. J.*, 1935, **29**, 1983), and of Potter and Elvehjem (*J. Biol. Chem.*, 1936, **117**, 341) with the enzyme from animal tissues may be mentioned. Notable also are the experiments of Hopkins, Morgan and LutwakMann (*Biochem. J.*, 1938, **32**, 1829) of Euler and Hellström (*British Chemical Abstracts* 1938, A, III, 438, 949; 1939, 623,) and of Bernheim (*J. Biol. Chem.*, 1940, **133**, 485) on the -SH-group of the enzyme, of Cook and Mapson (*Biochem. J.*, 1930, **24**, 1538) and Yudkin (*Biochem. J.*, 1933, **27**, 1849) on the properties of the enzyme in *B. coli* and of Stotz and Hartings (*J. Biol. Chem.*, 1937, **118**, 479) on the components of succinate-fumarate systems.

The properties of the enzyme from plant sources have not been studied as yet. The tendency of drawing any conclusion from the study of an enzyme in animal tissues and applying it t that of the plant system is dangerous, as Linderstrm-Lang (*Ann. Rev. Biochem.* 1937, **6**, 48) points out, because of the divergency often met with the same enzyme system from different sources. Thus Reichel and Neeff (*Z. physiol. Chem*, 1936, **240**, 163) reported that neither D. P. N. nor the flavin system is involved in the aerobic activities of citric dehydrogenase from liver while Wagner-Jauregg and Rauen (*Z. physiol. Chem.*, 1935, **237**, 227) found flavoprotein active under both aerobic and anaerobic conditions in the case of the corresponding enzyme from cucumber seeds. The oxidation products were quite different in the two cases and entirely different enzyme systems appear to be involved. A similar divergency is found between the action of α-glycerophosphate dehydrogenase from rabbit muscle (Green, *Biochem J.*, 1936, **30**, 629) and from cucumber seeds (Wagner-Jauregg and Rauen, *Z. physiol. Chem.*, 1935, **237**, 233).

Cucumber seed has proved to be the source of a host of different dehydrogenases, as is evidenced by the isolation from it of malic dehydrogenase by Thunberg (*Skand. Arch. Physiol.*, 1936, **73**, 67) and isocitrico, citrico and α-glycerophosphate dehydrogenases by Wagner-Jauregg and Rauen (*loc. cit.*). The occurrence of these enzymes led us to think of the possibility that a succinic dehydrogenase which is so widely distributed, may be found in this seed. Consequently, we tried to have an enzyme preparation by mincing cucumber seeds, washing with water to remove the water-soluble enzymes and then extracting with $M/15$ secondary sodium phosphate. The enzymic activity of the preparation was tested both anaerobically and aerobically, Using methylene blue as hydrogen acceptor in anaerobic experiments, according to Thunberg's technique, no decolourisation of the dye in presence of succinate ($M/100$) even after 4 to 6 hours was observed. Aerobically a large oxygen uptake (183/$\mu$l per 30 minutes) was found but in the blank too there was a large oxygen uptake (140/$\mu$l per 30 minutes). Dialysis of the extract prior to working with it could produce no significant change. Moreover, while in some preparations such oxygen uptake was found, in others there was very little oxygen absorption both in the control and the blank. Such properties as optimum $p_H$, optimum concentration of the substrate, temperature inactivation, action of narcotics and other inhibitors have been studied. Lastly a preliminary experiment was made on the active group of the enzyme on the line of Bernheim (*J. Biol. Chem.*, 1940, **138**, 485).

The cause of the observation that with some preparations practically no oxygen uptake took place has also been tested. It is found that for active enzyme preparations always fresh cucumber must be used. Preparations from fruits kept for 2—3 days after plucking are completely inactive.

## EXPERIMENTAL

In anaerobic experiments a series of Thunberg tubes were prepared each containing 0·5 c.c. of 2:6-dichlorophenol-indophenol (1/5000), 1 c.c. of the enzyme preparation and 0·5 c.c. of succinic acid (neutralised $M/10$ solution). The total volume was made up to 4 c.c. with phosphate buffer ($M/15$) so that the concentraton of the substrate stood at $M/80$, The tubes were then evacuated at the room temperature with the help of a Cenco Hyvac pump and the time for complete decolourisation of the dye was noted by placing the tubes in a bath at 38°.

Aerobic experiments were done in Warburg-Barcroft apparatus. One Barcroft vessel contained only the enzyme solution to find out the amount of oxygen absorbed without addition of the substrate. As mentioned before, the amount of oxygen absorbed in the blank was considerable and as such the number of aerobic experiments was limited. It must be mentioned that the oxidising capacity of the enzyme solution varied from sample to sample, and as such no comparison between results of different experiments was possible. Each experiment was, however, carried out with one and the same sample and generally at the same time.

The enzyme solution was prepared by grounding the washed seeds in a mortar with acid washed sand and extracting with $M/15$ secondary sodium phosphate. Ths extract was then pressed out of the muslin and the solution was used in anaerobic experiments. The whole process was carried out in the cold upon which the success depended.

In aerobic experiments, minced seeds were first washed with water and finally extracted with disodium phosphate as mentioned above. The solution was dialysed in parchment papers for 24 hours against distilled water and the dialysed clear solution was used. The results are given in Table I.

*Inactivation by Heat.*—3 C.c. of the enzyme solution were placed in a series of test tubes and kept immersed for 10 minutes in baths at different temperatures. The solution was then brought down to 30° and the dehydrogenase activity was measured anaerobically, as before. The results are given in Table III.

It will be seen from Table III that the activity of the enzyme remains intact even after heating to 40°. After that, there is a gradual decrease in activity, and at 60° the enzyme is completely inactivated, its reduction time being beyond that of the blank. Another point should also be noted. In separating fumarase from succinic acid dehydrogenase of animal tissues the usual procedure is to heat the enzyme solution to 50°, when fumarase is inactivated and the succinic acid dehydrogenase activity remains behind. A similar procedure adopted in the case of the plant enzyme, however, would be detrimental as along with the inactivation of the fumarase the cucumber succino dehydrogenase will also lose about 50% of its activity. In the experiments described, therefore, no such separation was attempted.

TABLE I

*Variation of activity with $p_H$*

Temp. = 38°

| $p_H$ of the medium. | Reduction time (T) | Activity (100 × 1/T) |
|---|---|---|
| 6·4 | 16 | 6·3 |
| 6·6 | 16 | 6·3 |
| 6·8 | 14 | 7·1 |
| 7·2 | 11 | 9·1 |
| 7·4 | 15 | 6·7 |
| 7·7 | 22 | 4·5 |
| 8·0 | 32 | 3·1 |

TABLE III

*Heat inactivation of the enzyme.*

| Temp of incubation. | Reduction time (T). | Activity (100/T). |
|---|---|---|
| 30° | 13 mins | 7·7 |
| 35° | 13 | 7·7 |
| 40° | 13 | 7·7 |
| 45° | 16 | 6·3 |
| 50° | 23 | 4·3 |
| 55° | 40 | 2·5 |
| 60° | 44 | Nil |

TABLE IV

*Action of narcotics on the dehydrogenase*

Temp. = 38°.

| Narcotic used. | Reduction time (A). | Reduction time of the control (B). | Percentage inhibition $\frac{100(1/B-1/A)}{1/B}$ |
|---|---|---|---|
| Vanillin (0·1%) | 20½ mins. | 18 mins | 12·2 |
| Urethane (1%) | 23 | ,, | 21·7 |
| Barbitone (1%) | 21¾ | ,, | 17·2 |
| Octyl alcohol (0·001%) | 24 | ,, | 25·0 |

In Table III time of decolourisation in the blank = 44 minutes.

In Table I the time of decolourisation of the blank was from 45 minutes to 1 hour and in some cases more. The optimum $p_H$ is thus 7·2, a value very near to that found with the dehydrogenase of animal tissues, the optimum $p_H$ of the latter being 7·4.

### *Optimum Substrate Concentration*

Table II shows the effect of substrate concentration on the activity of the enzyme.

TABLE II

Temp = 38°

| Tubes. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Enzyme (c.c.) | 1.0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 |
| Dye (c.c.) 1/5000 | 0·5 | 0·5 | 0·5 | 0·5 | 0·5 | 0·5 |
| Phos. buffer (c.c.) M/15 | 1·5 | 2·0 | 1·5 | 2·0 | 1·5 | 2·0 |
| Final conc. of succinic acid | M/40 | M/80 | M/160 | M/320 | M/640 | M/1280 |
| Reduction time (T) | 9·0 | 9·0 | 10·0 | 11·7 | 18·2 | 25·0 |
| Activity (100/T) | 11·1 | 11·1 | 10·0 | 8·6 | 5·5 | 4·0 |

*Action of Narcotics.*—Sen (*Biochem. J.*, 1931, **25**, 849) studied the action of a large number of narcotics such as vanillin, phenylurea, diethylurea, valeronitrile, propionitrile, ethylurethane and phenylurethane on succinodehydrogenase of the animal tissues. Because of the war most of the narcotics were not available. The concentration of the narcotics was so arranged that the activity fell from 10 to 30%. The results are given in Table IV.

In each of the tube were placed 2 c.c. of the enzyme, 0·5 c.c. of the substrate, 0·5 c.c. dye solution and 0·5 c.c. of the narcotic under question at the required concentration. The total volume was made to 4 c.c. by adding phosphate buffer of $p_H$ 7·2. The same enzyme solution was used throughout so that a comparison of the action of different narcotics was possible.

*Action of other Inhibitors.*—Stotz and Hastings (*J. Biol. Chem.*, 1937, **118**, 479) measured the inhibition of the succinic acid dehydrogenase produced by a number of different substances such as arsenite, arsenate, selenite, fluoride and potassium cyanide. They found that sodium selenite and potassium cyanide stopped respectively the dehydrogenating and oxidising function completely without affecting the other at all. Fluoride affected both the factors while pyrophosphate affected only the oxidase. Potter and Elvehjem (*J. Biol. Chem.*, 1936, **117**, 341) also studied the action of those substances upon this enzyme prepared from a homogeneous suspension of the chick kidney. They found almost similar results with arsenite, arsenate, selenite, and potassium cyanide. With fluoride, however, the inhibition was found to be practically nil. It seemed, therefore, of interest to see how these substances behaved with the plant enzyme. It was found that sodium pyrophosphate and fluoride affected both the aerobic and anaerobic activity while sodium arsenite and potassium cyanide affected only the oxidase factor. The results are shown in Tables V and VI.

TABLE V

*Action of inhibitors on anaerobic activity*

Temp. = 38°

| Inhibitor | Conc. | Reduction time (A). | Reduction time of control (B). | % inhibition $100\,\frac{(1/B-1/A)}{1/B}$ |
|---|---|---|---|---|
| Sodium pyrophosphate. | *M*/100<br>*M*/300<br>*M*/1000 | 32<br>26<br>19 | 16·5<br>16·5<br>16·5 | 48·4<br>36·5<br>13·2 |
| Sodium fluoride | *M*/100<br>*M*/300 | 22·5<br>20 | 17<br>17 | 24·4<br>15 |
| Sodium arsenite | *M*/100 | 18·2 | 18 | *Nil* |
| Potassium cyanide | *M*/100 | 19 | 19 | *Nil* |

TABLE VI

*Effect of inhibitors on aerobic activity*

Temp. = 38°

| Inhibitor. | Oxygen uptake in µl/ per 2 c c. enzyme soln per hr. | | | |
|---|---|---|---|---|
| | Control. | Conc. of the inhibitor. M/100. | M/300. | M/1000. |
| Sodium arsenite | 430 | 159 | 216 | 344 |
| Sodium arsenate | 395 | 301 | 329 | 398 |
| Sodium fluoride | 412 | 382 | 400 | 426 |
| Pot. cyanide | 420 | 6 | 43 | 134 |
| Sodium pyrophosphate | 412 | 251 | 310 | 380 |

TABLE VII

*Effect of copper sulphate on the enzyme*

Temp. = 38°

| Enzyme in c.c | Treatment of the enzyme. | $CuSO_4$ in c c $10^{-4}M$. | Phos buffer (c.c) | Water in c.c. | Substrate *M*/10 in c.c | Oxygen per hour. (µl) |
|---|---|---|---|---|---|---|
| 2 | — | — | 2 | 2 | 1 | 388 |
| 2 | Not incubated previously | 2 | 2 | — | 1 | 380 |
| 2 | Incubated for one hour | 2 | 2 | — | 1 | 0 |
| 2 | — | — | 2 | 2 | 1 | 370 |
| 2 | Not incubated previously | 0·5 | 2 | 1·5 | 1 | 369 |
| 2 | Incubated for one hour | 0·5 | 2 | 1·5 | 1 | 58 |

It will be seen from Table VI that potassium cyanide produces near about 100% inhibition at a concentration of 0·01 *M*. The action of arsenite upon the aerobic activity is also considerable being about 63% at a concentration of 0·01 *M*. In contrast to the action of arsenite, that of arsenate is consideraly small.

*On the -SH group of the Enzyme.*

Hopkins and Morgan (*Biochem. J.*, 1938, **32**, 611) showed that when washed and minced tissues are incubated anaerobically for adequate periods with solutions of glutathione (GSSG) at $p_H$ 7·4, the succinic acid dehydrogenase is completely inactivated. On the other hand the original activity of the enzyme is fully regained when the preparations, so treated, are subsequently re-incubated with the reduced form of glutathione (GSH). Hopkins *et al* (*Biochem. J.*, 1938, **32**, 1829) also studied the influence of other substances known or supposed to inhibit the enzyme by combining or reacting with the -SH group and also the influence of other substances in protecting the enzyme from such inactivation. The enzyme is inactivated by copper, maleic acid and iodoacetic acid, substances that react with the -SH group while malonic, succinic and fumaric acids protect the enzyme from inactivation by GSSG. Bernhein (*J. Biol. Chem.*, 1940, **133**, 485) studied the action of copper on the enzyme. The inhibitory action of copper on succinic acid dehydrogenase is the result of its catalytic effect on the oxidation of -SH group of the enzyme protein. It follows, therefore, that a concentration of copper which causes no inhibition immediately after its addition to the enzyme, should cause an inhibition if incubated for sufficient time before its activity is tested. On this principle, the action of copper sulphate on the plant enzyme was determined. Anaerobically the experiment could not be done since in presence of phosphate buffer, copper sulphate solution gives a precipitate of copper phosphate. Further, the addition 2 : 6-dichlorophenol-indophenol to it produces a pink colour which persists indefinitely. The same pink colour was obtained even without addition of the buffer. Aerobic experimenrs were, therefore, resorted to.

It was found that immediate addition of 2 c.c. of $10^{-4}$ *M* copper sulphate solution to a mixture of 2 c.c. of enzyme, 1 c.c. of substrate and 2 c.c. buffer (to make a total volume of 7 c c.) produced from 2 to 3% inhibition of the enzyme. (There was a slight oxidation of the copper sulphate in presence of the enzyme, probably due to its passage to a higher state of oxidation, which was carefully accounted for). Another 2 c.c. portion of the enzyme were first incubated for about an hour with the same volume of copper sulphate solution at the same concentration, and after the required time. phosphate buffer (2 c c.) and substrate (1 c.c.) were added and the activity was measured. There was no oxygen uptake indicating complete inactivation of the enzyme. Copper sulphate solution at a low concentration (0·5 c.c. of $10^{-4}$ *M* solution in a total volume of 7 c.c.) was also used in a second series of experiments. The result was similar but this time initial inactivation was practically nil whereas inactivation after one hour's incubation was about 70%. The result, represented in Table VII, is interesting and shows that the plant enzyme probably also contains the -SH group.

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# A NEW GROUP OF COLLOIDAL ELECTROLYTES

By N. R. Dhar and S. Ghosh

Some of the sols, *e.g.* silicic acid, vanadic acid, tungstic acid, molybdic acid, telluric acid, and antimonic acid which can be coagulated by electrolytes either in the absence of alkali or by the addition of traces of alkali, which makes them unstable towards coagulation, show high electric conductivity. In all these sols a part of the substance exists in the molecular condition and another part as polymerised molecules, capable of giving out complex ions, which are readily adsorbed by the sol particles

On dilution, simple molecules in the dissolved condition are produced from the polymerised and colloidal aggregates and thus the electrical conductivity increases with dilution All these properties show that these substances are typical colloidal electrolytes

Soaps, silicates, several dyestuffs, alkaline and acidic proteins, etc. are now considered as colloidal electrolytes. In this paper we are advancing evidence in favour of the view that silicic, vanadic, tungstic, molybdic, telluric and antimonic acids may be included in the category of colloidal electrolytes. Some of these conduct electricity fairly well and all of them behave as colloids.

### *Stability as Colloids*

We have investigated the coagulation of sols by potassium chloride in presence or absence of small amounts of alkali and the following results are obtained.

TABLE I

| Sols of acids. | Precipitation value of KCl without alkali. | Precipitation value of KCl with alkali | Amount of alkali added. | |
|---|---|---|---|---|
| Silicic | — | 0·900*M* | KOH | 0·0271*M* |
| Vanadic | 0·0129*M* | 0·0064 | $NH_4OH$ | 0·0133 |
| Tungstic | 0·0354 | 0·0125 | KOH | 0·0097 |
| Molybdic | 0·3300 | 0·1800 | $NH_4OH$ | 0·0160 |
| Telluric | 0·2800 | 0·0800 | NaOH | 0.0833 |

We have advanced the view in previous publications that the sols are composed of a certain amount of the substance in true molecular condition in the dissolved state existing as simple and polymerised molecules and the following equilibrium is likely to exist:—

$$\underset{\text{Simple molecules}}{n\mathrm{HA}} \rightleftharpoons \underset{\text{Polymerised molecules}}{(\mathrm{HA})_n} \rightleftharpoons \underset{\text{Colloid particles (negatively charged).}}{[(\mathrm{HA})_m x(n\mathrm{A})y\mathring{\mathrm{A}}]}$$

The electric charge on the colloid particles is chiefly due to the adsorption of $x$ polymerised anions carrying $n$ units of electric charge and $y$ simple anions each carrying one unit charge. The adsorption of the complex ions appear to be more important than that of the simple anions in the formation of the sol because of the greater amount of electric charge carried by the complex anions. The above view point is supported by the fact that small amounts of alkali render the sols unstable towards KCl although all of them are negatively charged. This behaviour is entirely different from that of sols like ferric hydroxide, chromium hydroxide, etc., which when prepared under ordinary conditions, are positively charged and they are rendered stable by the addition of $H^{\cdot}$ ions. This peculiar behaviour of the negatively charged sols of silicic, vanadic, tungstic acids etc. has been explained by us in the following manner. when an alkali is added to such a sol, it reacts with the simple molecules first and in order to restore the equilibrium more of the simple molecules are formed at the expense of the polymerised ones which give out complex negative ions. These negative complex ions are more responsible for the stabilisation of the sols than the simpler ions and as the alkali causes the removal of the complex anions, the sols are rendered unstable in their presence as shown in Table I. On the other hand, in presence of acids these sols are likely to be more stable as was shown by Schulz and Jander (*Z. anorg. Chem.*, 1927, **162**, 141) in the case of tungstic acid sol and by us in the case of vanadic acid sol.

### *Electrical Conductivity and other Properties of the Colloids*

*Silicic Acid Sol.*—Mylius and Groschuff (*Ber.*, 1906, **39**, 116) conclude that at the moment of formation of silicic acid by the action of acids on water glass, it exists in the molecular condition, which passes unchanged through a parchment dialyser. Colloidal particles then result from the polymerisation of the simple silicic acid molecules on keeping the solution and this is shown by the increase of molecular weight for many weeks. Several workers have concluded that this ageing process leads to the formation of highly polymerised colloid particles and finally to crystalline silica. We have also come to the same conclusion from our observation that silicic acid sol develops a marked increase in viscosity with time. It is generally believed that in the process of coagulation of sols there is an aggregation of colloidal particles and in this process there is usually an increase in their viscosity.

We have also investigated the change in the electrical conductivity of a dialysed sol of silicic acid (prepared by the hydrolysis of silicon tatrachloride) with time and the following results have been obtained.

TABLE II

Sol conc. = 6·17g. of $SiO_2$/litre. Temp. = 30°

| Date | 4-4-1927 | 2-5-1927 |
|---|---|---|
| Specific conductivity | $5{\cdot}75 \times 10^{-6}$ | $6{\cdot}10 \times 10^{-6}$ |

*Tungstic Acid Sol.*—This sol, obtained according to the method of Graham by adding an acid to sodium tungstate solution, rapidly passes through a parchment paper and it is well known that this optically clear sol contains a large percentage of the acid in the molecular state. We prepared tungstic acid sol by first precipitating the substance by the action of an excess of hydrochloric acid on sodium tungstate at 8° and the sodium chloride and the excess of hydrochloric acid removed by washing the precipitate, which gradually passed into a sol. The sol was further purified by dialysis, when some tungstic acid appeared in the dialysate. The pure sol, free from chloride ions, was found still to contain appreciable amounts of tungstic acid, which did not coagulate by electrolytes like KCl, $KNO_3$, etc. The electrical conductivity of the sol was fairly high and it was distinctly acidic ($H^{\cdot}$ ion conc. $=10^{-3}$). The influence of ageing on the electric conductivity was also determined and the following results were obtained.

TABLE III

| Date | 22-10-1927 | 31-10-1927 | 2-11-1927 | 4-11-1927 | 18-11-1927 |
|---|---|---|---|---|---|
| Sp. conducty. $\times 10^3$ | 4·12 | 3·883 | 3·769 | 3·728 | 3·632 |

The equivalent conductivity of tungstic acid was determined by Sobolew (*Z. anorg. Chem.*, 1896, **12**, 169) and the following are his results,

TABLE IV

Temp. $=24°$

| $v$ | ... | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|
| $\lambda$ | ... | 176·4 | 233·5 | 279·1 | 325·1 | 371·6 | 416·7 |

These results prove that an appreciable amount of tungstic acid remains in the dissolved condition as simple and polymerised molecules, which dissociate into hydrogen ions and a negative ion. A decrease in the specific conductivity on ageing is obviously due to the formation of more of polymerised molecules and the colloidal aggregates with time.

*Molybdic Acid Sol*.—Rosenheim and Bertheim (*Z. anorg. Chem.*, 1903, **34**, 427) have reported that the dihydrate of molybdenum trioxide has a definite solubility and the acid diffuses through a parchment paper and possesses the molecular weight of 600. We have carefully studied this sol obtained by the interaction of hydrochloric acid and ammonium molybdate. As the sol is allowed to dialyse, a large percentage of the molybdic acid passes through the parchment paper. With time the portion of the acid existing as simple molecules gradually polymerises and finally forms colloid aggregates as will be evident from the following results on the ultrafiltration of the sol obtained by us.

TABLE V

$MoO_3$ in 100 c.c of the sol $=$ 1·550 g.

| Time (hr.) ... .. ... | 2 | 24 | 48 | 72 | 96 | 120 |
|---|---|---|---|---|---|---|
| $MoO_3$ in 100 c.c of the filtrate (g.) ... | 0·740 | 0·732 | 0·726 | 0·714 | 0·706 | 0·700 |
| $MoO_3$ as colloid in 100 c c of the sol (g.) .. | 0·810 | 0·818 | 0·824 | 0·832 | 0·840 | 0·846 |
| % present as colloid. ... ... ... | 52·2 | 52·77 | 53·16 | 53·67 | 54·19 | 54·59 |

In Table VI the results are recorded to show considerable diminution of percentage of the colloid on dilution of the sol.

TABLE VI

| Sol. conc | $MoO_3$ in 100 c.c of the sol. | $MoO_3$ in 100 c.c of the filtrate. | $MoO_3$ as colloid in 100 c c of the sol. | % of colloid |
|---|---|---|---|---|
| 2% | 1·55 g. | 0·740 g. | 0·810 g. | 52·2 |
| 1 | 0·775 | 0·508 | 0·267 | 34·4 |
| 0·5 | 0·3875 | 0·296 | 0·0915 | 23·9 |

A dialysed sol of molybdic acid and freed from the impurities shows an appreciable electrical conductivity and distinct acidity which decrease with time (Table VII).

TABLE VII

| Date ... | 27-12-28 | 31-12-28 | 4-1-29 |
|---|---|---|---|
| Sp. condy. at 30° $\times 10^3$ ... | 1·719 | 1·676 | 1·660 |

The following results were obtained by Grossmann and Krämer (*Ber.*, 1903, **36**, 1606) on the molecular conductivity of a solution of dihydrated molybdenum trioxide.

TABLE VIII

| $v$ | ... | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ | ... | 95·8 | 129·5 | 147·5 | 155·6 | 160·6 | 163·6 | 169·0 |

*Vanadium Pentoxide Sol.*—Several years ago Dumanaski (*Kolloid Z.*, 1923, **33**, 147) showed that the composition of the colloidal aggregates of vanadium pentoxide sol has the formula of $[H_2V_6O_{17}(V_2O_5)_5]''$. We have found that an appreciable amount of vanadic acid is present in the molecular state in a sol of vanadium pentoxide, which cannot be precipitated by an electrolyte and that this amount decreases appreciably with time.

The electrical conductivity of a dialysed vanadium pentoxide sol decreases with the ageing of the sol as given in the following table.

TABLE IX

Sol conc. $= M/180$.

| Date ... ... | 10-4-22 | 9-5-22 | 22-6-22 | 9-9-22 |
|---|---|---|---|---|
| Mol conductivity at 30° .. | 113·4 | 91·5 | 85·1 | 83·8 |

Vanadium pentoxide sol, therefore, shows a high electrical conductivity and contains some of the substance in the dissolved state, which gives out ions. The simple molecules gradually aggregate forming polymerised molecules and finally polymerised molecules form still larger aggregates producing the particles of colloidal dimension.

*Telluric Acid.*—Rosenheim and Jander (*Kolloid Z.*, 1918, **22**, 23) have concluded that a solution of telluric acid behaves as a semi-colloid. We have investigated the colloidal property of this acid and have found that the acid is not coagulated by such electrolytes as KCl, NaCl, LiCl, RbCl etc. but the sol becomes unstable and can be coagulated by these electrolytes in the presence of traces of an alkali. These results are analogous to the behaviour of a silicic acid sol Similarly Behren and Traube (*Z. physikal. Chem.*, 1930, **146**, 1) have reported on the colloidal behaviour of telluric acid. Moreover, irregularities in the boiling point measurement indicate the formation of some colloidal telluric acid.

We have observed that on dialysis practically all telluric acid passes through the parchment paper and this is due to the fact that the tendency of this acid to form simpler products is very prominent with dilution.

Rosen and Jander (*loc cit.*) have determined the electrical conductivity of telluric acid at 30° and their results are reproduced below.

TABLE X

| $v$ ... | 4 | 8 | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|---|---|
| $\lambda$ . | 0·1902 | 0·1984 | 0·2029 | 0·2119 | 0·2245 | 0·2611 | 0·3131 | 0·4460 | 0·6913 |

The electrical conductivity of $H_2S$ is greater than that of telluric acid, which is weaker than $H_2S$ as an acid.

We have also studied the change in the electrical conductivity of the sol of telluric acid with time and the following are our results.

TABLE XI

Conc. of telluric acid $= 100$ g./litre.

| Time (days) .. | — | 5 | 10 |
|---|---|---|---|
| Sp. conductivity × $10^4$ ... | 0·773 | 0·773 | 0·775 |

The hydrogen ion concentration of 100 g. of the sol per litre is $10^{-5.8}$ showing that it is a very weak acid.

*Antimonic Acid Sol.*—Delacroix (*Bull. Soc. Chim.*, 1899, *iii*, **21**, 1049), and Senderens (*ibid.*, p. 47) believed that the product obtained by the hydrolysis of antimony pentachloride existed in the state of true solution. Jander (*Kolloid Z.*, 1918, **23**, 1822) reported it to be a semi-colloid. We have studied the colloidal behaviour of antimonic acid obtained by first precipitating antimonic acid from potassium antimonate by nitric acid and then peptising the sol by washing off the electrolytes. The sol was further purified by dialysis when a slightly turbid negatively charged sol of antimonic acid was obtained. A considerable amount of antimonic acid passed out through a parchment paper and some acid, which cannot be coagulated by electrolytes like KCl, $KNO_3$ etc., remained showing that a certain amount of this acid exists in the molecular form. We have also shown that the acid remaining in the molecular form consists mostly of simple molecules. Hence the sol does not become appreciably unstable by traces of an alkali. This view is further confirmed by our results on the change of electrical conductivity of antimonic acid sol due to ageing (Table XII).

TABLE XII

Sol conc. = 0·95 g./litre.

| Date | ... | 15-8-28 | 20-8-28 | 30-8-28 | 13-9-28 |
|---|---|---|---|---|---|
| Sp. condy. $\times 10^3$ | ... | 3·06 | 3·00 | 3·02 | 2·98 |
| $p_H$ | ... | 4·2 | — | — | 4·3 |

We have observed that the sols of antimonic acid, when coagulated by monovalent electrolytes like KCl, NaCl, can be reconverted into the sol state by washing them with water. These sols therefore, resemble the typical lyophillic sols *e.g.* gelatine, soap, etc. in this respect.

From the Tables IV, VIII and X we observe that the molecular conductivity of the sols of telluric, molybdic and tungstic acids increases with dilution showing that more and more of simple molecules are being formed at the expense of the polymerised molecules and the colloidal particles on dilution. Our experimental results given in Table VI with molybdic acid show that the percentage of colloidal molyblic acid decreases with the increasing dilution of the sol.

It is interesting to note in the following table that the molecular conductivities of $LiIO_3$, $CdCl_2$, $CdBr_2$ $CdI_2$ and $H_2Cd\,I_4$ at 18° increase markedly with dilution.

TABLE XIII

| Conc. | LiCl. | $BaCl_2$. | $LiIO_3$. | $CdCl_2$. | $CdBr_2$. | $CdI_2$. | $H_2CdI_4$. |
|---|---|---|---|---|---|---|---|
| 0·0001 *M* | 98·1 | — | 66·7 | — | — | — | — |
| 0·0005 | 97·2 | 117·0 | 65·9 | — | — | — | — |
| 0·001 | 96·5 | 115·6 | 65·3 | — | 99·0 | 92·0 | 204 |
| 0·005 | 93·9 | — | 62·9 | 91·0 | 86·5 | 76·7 | 186 |
| 0·01 | 92·1 | 106·7 | 61·2 | 83·0 | 76 3 | 65 6 | 169 |
| 0·05 | 86·1 | 96·0 | 55·3 | 59·0 | 53·2 | 40·1 | 128 |
| 0·10 | 82·4 | 90·8 | 51·5 | 50·0 | 44·6 | 31·0 | 113 |
| 0·50 | 70·7 | 77·3 | 39·0 | 30 8 | 25·2 | 18·3 | 89 |
| 1·00 | 63·4 | 70·1 | 31·2 | 22 4 | 18·3 | 15·4 | 82 |

The molecular conductivities of LiCl and $BaCl_2$ have been incorporated in the above table for comparison. It is well known that the cadmium salts and iodates exist partly in the polymerised form in solution, and it is to be concluded from the table that at higher concentrations the polymerised molecules of these salts rapidly increase in number.

In the following table some of the results of Harman (*J. Phys. Chem.*, 1925, **29**, 1155) on the equivalent conductivities of sodium silicates are given.

TABLE XIV

| | $v=1$ | 10 | 100 |
|---|---|---|---|
| ½ $Na_2SiO_3$ | 85·57 | 157·5 | 193 |
| ½ $Na_2Si_2O_5$ | 81·25 | 130·8 | 155 |
| ½ $Na_2Si_8O_{17}$ | 23·24 | 57·8 | 81·5 |

We are of opinion that the rapid change in the equivalent conductivities of the polysilicates $Na_2Si_2O_5$ and $Na_2Si_8O_{17}$ on dilution is due to the formation of more of simple anions at the lower concentration of the silicates. Thus

$$Na_2Si_2O_5 + H_2O \longrightarrow Na_2SiO_3 + H_2 SiO_3$$
$$Na_2SiO_3 \longrightarrow 2\, Na^{\cdot} + SiO_3{}''$$

Similar results were obtained by Biltz and Vegesack (*Z. physikal. Chem.*, 1910, **73**, 481) for the equivalent conductivity of the sol of Congo red, which is the sodium salt of a dibasic acid.

TABLE XV

Temperature = 25°

| Dilution | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| Equiv condy. | 58·7 | 64·3 | 71·0 | 79·3 | 87·6 | 96·1 |

McBain and co-workers (*J. Chem. Soc.*, 1919, **115**, 1279, 1300) have reported that the molecular conductivity of soap solutions at first rapidly decreases then increases to pass through a maximum with increasing concentrations.

## DISCUSSION

It is well known that the specific conductivity of well dialysed colloids is slightly greater than that of the water used as a medium (*vide* Walden, "Das Leitvermogen der Losungen". 1924, p. 320). A dialysed sol of silicic acid prepared by Kohlrausch (*Weid. Ann.*, 1893, **50**, 133) had the specific conductivity of $11{\cdot}3 \times 10^{-5}$. One of the sols prepared by us by the hydrolysis of silicon tetrachloride gave a specific conductivity of $5{\cdot}75 \times 10^{-5}$ at 30°. It is well known that the heat of neutralisation of silicic acid by an alkali is 5230 cals. against $H_2S$ with 7800 cals. and carbonic acid with 20,180 cals., showing that silicic acid is an extremely weak acid. Hence its conductivity due to its acid character is exceedingly small and it is practically impossible to draw any conclusion regarding its state of polymerisation from the electrical conductivity measurements. Telluric acid behaves in the same way as silicic acid. As the inherent electrical conductivity of these sols is so small, ageing, which may cause polymerisation, is not likely to show a decrease in the electrical conductivity but may lead to a small increase in the electrical conductivity due to the release of the adsorbed ions like $H^{\cdot}$, $Cl'$ etc., and this behaviour has actually been observed with silicic and telluric acid sols. In this respect these sols behave like the sols of ferric hydroxide, aluminium hydroxide etc. On the other hand, the sols of vanadic, molybdic, tungstic and antimonic acids being stronger acids are much more electrically conducting and the effect of ageing on these sols is chiefly characterised by the polymerisation of the simple molecules causing a decrease in the electrical conductivity with time.

The foregoing observations show that antimonic, vanadic, tungstic and molybdic acids behave like the typical colloidal electrolyte, soap, studied by McBain and co-workers (*loc. cit.*).

It appears, that a colloidal electrolyte is obtained from such a sol, which contains a part of the same substance as ionisable simple and complex molecules. The electrical charge on the colloid particles originates mainly from the adsorption of the complex anion, and the ions obtained from the simple and polymerised molecules are responsible for the high electrical conductivity of the sol. In the case of such sols as those of $Fe(OH)_3$, $Al(OH)_3$, $Zr(OH)_3$ etc. the electrical charge on the colloid particles is due to the preferential adsorption of an ion from an electrolyte, which is an impurity in the sol and can be removed by dialysis. The general scheme of the formation of the two types of colloids is, therefore, identical; in the first case the stabilising electrolyte is obtained from the dissolution of the dispersed particles arising from the same substance; whilst in the second case, the peptising substance is an electrolyte added to or formed in the medium during the formation of the sol. The view advanced in this paper regarding the nature of the colloidal electrolytes forms a part of the micellar theory of the constitution of the colloids as advanced by Pauli and others.

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# BIGUANIDE SULPHATE AS A REAGENT FOR THE ESTIMATION OF NICKEL

By Anil Kumar Majumdar

Nickel has been estimated volumetrically using biguanide sulphate which forms insoluble co-ordination compound with nickel

Biguanide and its substitution products are known to form characteristic co-ordination compounds with bivalent metals like copper, nickel, cobalt, etc.*.

Ray and Saha (*J. Indian Chem. Soc.*, 1937, **14**, 670), after a detailed study, have concluded that these compounds are of the type of inner-metallic complexes and thus account satisfactorily many of their properties such as strong colour, low solubility, etc.

Ray and Raychowdhury (*J. Indian Chem. Soc.*, 1941, **18**, 149) used biguanide sulphate as a reagent for the estimation of copper. The present author finds that nickel also can be estimated volumetrically after precipitation as nickel biguanide hydroxide, which is practically insoluble in water specially in presence of alkali.

The method permits the separation of nickel from other metals such as beryllium, zinc, iron, aluminium, chromium, titanium, uranium, arsenic, antimony and bismuth in presence of alkaline tartrate.

Biguanide sulphate precipitates nickel in presence of alkali as a yellow silky precipitate of the composition $[Ni\ (C_2N_5H_7)_2]\ (OH)_2$. It cannot be directly weighed as it loses weight during heating and absorbs carbon dioxide from air. Cobalt, copper. palladium, etc., which give. complexes with the reagent in presence of alkali must be absent so also manganese, magnesium, cadmium, tin and silver which are precipitated as oxides. Anions, *e.g.*, $PO_4'''$, $FeCy_6'''$,$FeCy_6''''$ etc. which give precipitate with $Ni^{++}$ ion and metals like calcium, barium, strontium and lead which give precipitate of sulphates should also be absent.

## EXPERIMENTAL

*Preparation of the Reagent Biguanide Sulphate.*—It was prepared from dicyanodiamide and ammonium iodide according to the method described by Ostrogovich (*Chem. Zentbl.*, 1910, II, 1890).

*Procedure.*—A nickel sulphate solution was prepared from Kahlbaum's reagent quality cobalt-free sample and standardised by means of dimethylglyoxime. To an acid solution, containing a known amount of nickel, was added an excess of 1% solution of the reagent biguanide sulphate (1 g. of biguanide sulphate in 100 c.c. water and made faintly ammoniacal). If the solution contains other elements such as chromium, beryllium, iron, aluminium, titanium, uranium, etc. a few grams of Rochelle salt, sufficient to hold these metals in solution, should be previously added. The solution was then cooled and then an excess of 2*N* caustic soda was added to it dropwise with stirring.

The nickel biguanide sulphate first precipitated changed with the excess of alkali into silky, yellow, crystalline precipitate of the base having the composition $[Ni\ (C_2N_5H_7)_2](OH)_2$. A few c.c. more of caustic soda were added to the solution. In presence of zinc a large excess of alkali should be added to form zincate. The solution was then allowed to settle in the cold, filtered and washed with minimum quantity of cold water till free from alkali. The precipitate was then transferred by hot water and dissolved in a measured quantity of standard sulphuric acid and the excess acid was titrated at room temperature with standard alkali using Wesselow's indicator.

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*Rathke (*Ber.*, 1879, **12**, 779), Emich (*Monatsch.*, 1883, **4**, 395); Smolka and Friedrich (*ibid.*, 1888, **9**, 227), Ziegelbauer (*ibid.*, 1896. **17**, 648); Andreasch (*ibid.*, 1927, **48**, 145), Ray and Bagch (*J. Indian Chem. Soc.*, 1939, **16**, 617).

The calculation is based on the following reaction:

$$[\mathrm{Ni}\,(\mathrm{C_2N_5H_7})_2]\,(\mathrm{OH})_2 + 2\mathrm{H_2SO_4} = \mathrm{NiSO_4} + (\mathrm{C_2N_5H_8^+})_2\mathrm{SO_4} + 2\mathrm{H_2O}$$

$$\mathrm{H_2SO_4} = \frac{\mathrm{Ni}}{2} \text{ or 1 c.c. } N\text{-}\mathrm{H_2SO_4} = 0{\cdot}0146725 \text{ g. of Ni.}$$

TABLE I

| Ni (g.) |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| (taken) | 0·01107 | 0·01107 | 0·01107 | 0·01549 | 0·01549 | 0·02214 | 0·02214 | 0·02214 | 0·02878 | 0·02878 |
| (found) | 0·01102 | 0·01109 | 0·01108 | 0·01550 | 0·01558 | 0·02203 | 0·02211 | 0·02215 | 0·02865 | 0·02875 |

TABLE II

Separation of Ni from Al.

|  | Taken. | Found. |
|---|---|---|
| Ni : | 0·0201 g. | 0·02014 g |
| Al : | 0·1843 | — |
| Ni : | 0·0201 | 0·02014 |
| Al: | 0·009215 | — |
| Ni : | 0·0201 | 0·02021 |
| Al : | 0·009215 | — |
| Ni: | 0·0201 | 0·02006 |
| : N | 0·01843 | — |
| : | 0·0201 | 0·02017 |
| Al: | 0·05529 | — |
| Ni: | 0·0201 | 0·02006 |
| Al, | 0·05529 | — |

Separation of Ni from U.

|  | Taken. | Found. |
|---|---|---|
| Ni: | 0·0201 g. | 0·02008 g. |
| U: | 0·0227 | — |
| Ni: | 0·0201 | 0·02011 |
| U: | 0·0454 | — |
| Ni : | 0·0201 | 0·02008 |
| U: | 0·0681 | — |

Separation Ni from Zn:

|  | Taken. | Found. |
|---|---|---|
| Ni. | 0·0201 g | 0·02014 g |
| Zn | 0·11 | — |
| Ni. | 0·0201 | 0·02021 |
| Zn: | 0·055 | — |
| Ni | 0·0201 | 0·02021 |
| Zn: | 0·11 | — |

Separation of Ni from Fe.

|  | Taken. | Found. |
|---|---|---|
| Ni | 0·0201 g. | 0·02021 |
| Fe | 0·0510 g. | — |
| Ni. | 0·0201 | 0·02021 |
| Fe: | 0·1020 | — |
| Ni: | 0·03015 | 0·03028 |
| Fe: | 0·0510 | — |
| Ni: | 0·0201 | 0·02014 |
| Fe. | 0·1020 | — |

Separation ot Ni from Be.

|  | Taken. | Found. |
|---|---|---|
| Ni. | 0·0201 | 0·02021 |
| Be· | 0·02 | — |
| Ni· | 0·0201 | 0·02021 |
| Be. | 0·01 | — |
| Ni· | 0·0201 | 0·02014 |
| Be· | 0·04 | — |

Separation of Ni from Ti.

|  | Taken. | Found. |
|---|---|---|
| Ni | 0·0201 | 0·02008 |
| Ti. | 0·0267 | — |
| Ni | 0·0201 | 0·02015 |
| Ti | 0·01335 | — |
| Ni. | 0·0201 | 0·02015 |
| Ti. | 0·0534 | — |

Separation of Ni from Cr.

|  | Taken. | Found. |
|---|---|---|
| Ni: | 0·0218 g. | 0·02170 g |
| Cr | 0·009885 | — |
| Ni: | 0·0218 | 0·02179 |
| Cr: | 0·01977 | — |
| Ni: | 0·0218 | 0·02177 |
| Cr. | 0·03954 | — |

The method possesses certain advantages in that the reagent can be easily and cheaply prepared.

My best thanks are due to Prof. P. Rây for his kindly suggesting me this problem and for the facilities received in working this piece of work in his laboratories.

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# COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART VII. COPPER, NICKEL AND COBALT(OUS) ETHYLENE-DIBIGUANIDE SALTS. COBALTOUS BIGUANIDINIUM SULPHATE AND HYDROXIDE

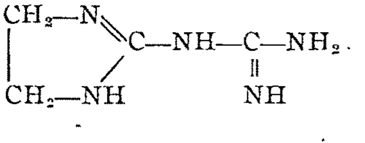
By Priyadaranjan Rây and Sailaja Prasad Ghosh

With a view to examine the nature of planar copper and nickel complxes, ethylenedibiguanide, presumably a quadridentate molecule, was employed as a co-ordinating addendum Evidences for *cis-trans* isomerism have previously been obtained in the case of copper and nickel phenylbiguanidinium complexes by one of us. A large number of copper and nickel ethylenedibiguanidinium salts, namely, chloride, bromide, iodide, sulphate, thiosulphate, thiocyanate, nitrate and nitrite, have been described. In no case, however, any indication of isomerism has been obtained, only one modification, the *cis*, being possible for such a quadridenate co-ordinating unit Incidentally, Dubsky's ethylenebiguanide (bidentate) has proved to be a dibiguanide.

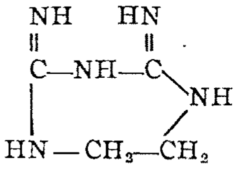
Contrary to Dübsky and co-workers' (*Collection*, 1938, **10**, 112) statement a fairly stable cobaltous ethylenedibiguanidinium sulphate has been prepared and its properties studied Cobaltous complexes with the simple biguanide, such as the sulphate, hydroxide and the anhydro-base, which were not previously studied, have also been described.

In Part III of this series copper and nickel phenylbiguanidines and their different modifications have been described (Rây and Chakravorty, *J. Indian Chem. Soc.*, 1941, **18**, 609). More or less definite evidences regarding *cis-trans* isomerism in the case of nickel phenylbiguanidine and probable indication of the same for the complex copper base and a number of its salts were obtained. Ethylenedibiguanide, which behaves as a quadridentate molecule with four units of attachment, should, therefore, give only the *cis* planar complexes with four co-ordinating central atoms, as ethylenediamine part of the molecule would always occupy adjacent positions. With this end in view, the preparation and study of the copper and nickel ethylenedibiguanide complexes were undertaken.

Dübsky, Langer and Strand (*loc. cit.*) have shown that the structure of ethylenebiguanide should be represented by the unsymmetrical formula (I) in preference to the symmetrical form (II) (Dittler, *Monatsh*, 1908, **29**, 645), as the latter, giving a seven-membered ring, would obviously be unstable.

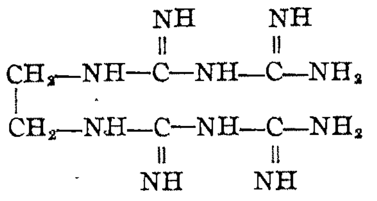


(I)



(II)

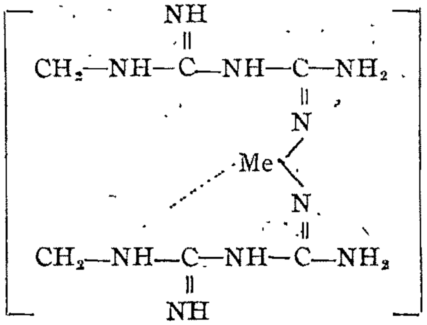
Chakravorty and Rây in this laboratory have, however, proved that the compound has a different composition and should be represented by the constitution (III), which would behave as a four co-ordinating unit (to be shortly published). Strictly speaking, the substance should be named ethylenedibiguanide (*cf. m*-phenylenedibiguanide, Rây and Siddhnata, *J. Indian Chem. Soc.*, 1943, **20**, 200).



$$\begin{array}{l} \qquad\qquad\;\; NH \qquad\;\; NH \\ \qquad\qquad\;\; \| \qquad\quad\;\; \| \\ CH_2{-}NH{-}C{-}NH{-}C{-}NH_2 \\ | \\ CH_2{-}NH{-}C{-}NH{-}C{-}NH_2 \\ \qquad\qquad\;\; \| \qquad\quad\;\; \| \\ \qquad\qquad\;\; NH \qquad\;\; NH \end{array}$$

(III)

Following the formulation suggested by Rây and his co-workers in previous papers for metal-biguanide complexes, the structure of copper and nickel ethylenedibiguanide compounds is represented by the formula IV.



$X_2$, where Me = Cu or Ni ;
X = any anion.

(IV)

Dübsky and co-workers (*loc. cit.*) have described only the corresponding insoluble copper and nickel ethylenebiguanide sulphate. In the present paper a large number of other salts will be discussed. Attempts to prepare the free bases led to rather impure products. As could be expected, no indication of the formation of isomeric modifications was obtained in either case. The colour and the diamagnetic character of the nickel complex, however, definitely indicate its planar structure with $d$-$s$-$p^2$ hybrid bonds.

The same authors have stated that cobalt, unlike copper and nickel, does not combine with ethylenebiguanide to form any co-ordination complex. A yellow precipitate obtained with ordinary cobalt salt solution was attributed by them to the presence of nickel as an impurity in the cobalt salt. This is, however, wrong and does not present the actual facts. For, we have succeeded in preparing cobaltous ethylenedibiguanide sulphate in the form of bright yellow, silky, crystalline precipitate from nickel-free cobalt salt solution. Cobaltous complexes are usually unstable and readily change into the cobaltic type. But the present compound was found to be quite stable and resembles the corresponding nickel complex in its general properties. No other salt, besides the sulphate, could, however, be prepared. The stability of the sulphate, therefore, appears to be due to its high degree of insolubility. On treatment with alkali it changes into a pale yellow product—the free complex base in a more or less impure state. On boiling with water it suffers oxidation forming a red solution of a cobaltic complex. Double decomposition of the sulphate with soluble barium salts led to the formation of oxidised products like hydroxo-aquo-cobaltic-ethylenedibiguanide salts.

Though the formation of complex cobaltous biguanide base has been referred to in a previous paper (Rây and Ghosh, *J. Indian Chem. Soc.*, 1942, **19**, 4), its preparation in a pure state, as well as that of the corresponding sulphate, along with their properties remain to be described here. They resemble the corresponding nickel compounds in colour; the sulphate is, however, decomposed readily by warm water with separation of green cobaltous hydroxide. Even water at room temperature leads to gradual decomposition. This can be represented as a case of hydrolysis.

$$[Co(BigH^+)_2]SO_4 + 4H_2O = [(H_2O)_2.Co.(OH)_2] + (BigH)_2.H_2SO_4.$$

Formation of the green hydroxide by the hydrolysis of a fourfold cabaltous complex suggests that the green modification of cobaltous hydroxide should be preferably represented as diaquo-dihydroxo-cobalt with no free ionic hydroxyl groups.

The magnetic moment of all the cobaltous complexes described above are considerably lower than that of the simple cobaltous salts or of the associated cobaltous complexes. They are to be regarded, therefore, as penetration complexes having planar configuration with *d-s-p*$^2$ hybrid bonds. The magnetic measurements will be described in a separate paper.

## EXPERIMENTAL

### *Copper Ethylenedibiguanidinium Salts*

*Sulphate.*—An intimate mixture of equimolecular quantities of ethylenediamine hydrochloride (8 g.) and dicyandiamide (5 g.) was fused between 140°-150°. The product was dissolved in water, filtered and the solution concentrated to eliminate the unreacted dicyandiamide which separated out. The filtrate was then precipitated with a solution of copper sulphate. The rose-red crystals of copper ethylenedibiguanide sulphate were first washed thoroughly with cold water, then with alcohol and finally dried in air. {Found: N, 32·40; $SO_4$, 22·32; Cu, 14·71. $[CuEn(BigH^+)_2]SO_4.2\frac{1}{2}H_2O$ requires N, 32·43; $SO_4$, 22·24; Cu, 14·73 per cent}. $En(BigH)_2$ = a molecule of ethylenedibiguanide, $C_6N_{10}H_{16}$.

The substance is almost insoluble in water, unaffected by dilute acids. Strong acids lead to its decomposition with formation of simple copper salts. Alkalis liberate the free complex base. This compound corresponds to that described by Dubsky and co-workers as well as by Dittler (*loc. cit.*).

*Chloride.*—An aqueous suspension of the crude copper ethylenedibiguanidinium hydroxide, obtained by digesting the complex sulphate with caustic soda solution, was treated with ammonium chloride. On cooling the red solution, rose-red needle-shaped crystals of the chloride separated. These were purified by recrystallisation from hot water. The product was washed and dried as usual. {Found: N, 36·10; Cl, 18·30; Cu, 16·45. $Cu[En(BigH^+)_2]Cl_2.1\frac{1}{2}H_2O$ requires N, 36·03; Cl, 18·25; Cu, 16·36 per cent}.

*Equivalent conductivity at 32°.*

| | | | | | | |
|---|---|---|---|---|---|---|
| $v$(litres) | ... | 64 | 128 | 256 | 512 | 1024 |
| $\Lambda v$ | ... | 114·9 | 119·4 | 123·4 | 126·9 | 131·1 |

$\Lambda_\infty$(mean) = 134·6, from Walden's formula, $\Lambda_\infty = \Lambda_v\,(1 + n_1.n_2.0{\cdot}692.v^{-\frac{1}{2}})$, where $n_1$ and $n_2$ are the valencies of the ions.

Hence the equivalent mobility of the complex $[CuEn(BigH^+)_2]$ ion is equal to 134·6 − 85·0 = 49·6, 85·0 being the mobility of Cl-ion at 32°. For copper biguanidinium chloride, $\Lambda_\infty$ was found to be 144·6 at 35° by Rây and Bagchi (*J. Indian Chem. Soc.*, 1939, **16**, 617); from which the equivalent conductivity for $[Cu(BigH^+)_2]$ ion is 144·6 − 89·2 = 55·4 at 35°, 89·2 being the mobility of Cl-ion at that temperature. On making corrections for the temperature difference it appears that the mobility of copper ethylenedibiguanidinium ion is only slightly lower than that of copper biguanidinium ion, which is to be expected.

*Bromide* was prepared by using ammonium bromide in the same way as the chloride. The product was purified by thrice recrystallisation from water. It forms silky, rose-red crystals, comparatively less soluble than the chloride. {Found: Br, 33·40; Cu, 13·25. $[CuEn(BigH^+)_2]Br_2.1\frac{1}{2}H_2O$ requires Br, 33·47; Cu, 13·31 per cent}.

*Iodide* was prepared by using ammonium iodide in the same way as the chloride or bromide. The deep purple solution on cooling deposited pink coloured needles of the iodide. These were recrystallised twice from water and dried in air. The crystals were moderately soluble in alcohol. {Found: I, 44·26; Cu, 11·18. $[CuEn(BigH^+)_2]I_2.1\frac{1}{2}H_2O$ requires I, 44·43; Cu, 11·13 per cent}.

*Thiosulphate*.—The complex thiosulphate was obtained as a voluminous rose-red precipitate on mixing a solution of the complex chloride with that of sodium thiosulphate. {Found: S, 14·30; Cu, 14·28. $[CuEn(BigH^+)_2]S_2O_3.2\frac{1}{2}H_2O$ requires S, 14·30; Cu, 14·20 per cent}.

*Thiocyanate* was obtained as a deep pink coloured crystalline precipitate by adding a concentrated solution of potassium thiocyanate to that of the complex chloride. The substance is moderately soluble in alcohol and water. {Found: S, 14·86; Cu, 14·80. $[CuEn(BigH^+)_2](SCN)_2.1\frac{1}{2}H_2O$ requires S, 14·76; Cu, 14·67 per cent}.

*Nitrate* was prepared by the action of ammonium nitrate on the aqueous suspension of the complex base. From the pink solution, on cooling, silky rose-red needles of the nitrate separated out. These were purified by recrystallisation from hot water. {Found: Cu, 14·35; $NO_3$, 28·18. $[CuEn(BigH^+)_2](NO_3)_2.1\frac{1}{2}H_2O$ requires Cu, 14·40; $NO_3$ 28·08 per cent}.

*Nitrite* was obtained by adding a strong solution of sodium nitrite to that of the complex chloride in the cold. It forms pink coloured crystals, soluble in water. {Found: Cu, 15·56; $NO_2$ (gas volumetrically as $N_2$), 22·50. $[CuEn(BigH^+)_2](NO_2)_2.1\frac{1}{4}H_2O$ requires Cu, 15·52; $NO_2$, 22·47 per cent}.

*Copper Ethylenedibiguanidine*.—When a solution of the pure complex chloride was treated with dilute ammonia, a light rose-red precipitate of the base was obtained This was washed with ice-cold water and dried in air, free from $CO_2$. {Found: N, 45·80; Cu, 20·36. $[Cu\,En(Big)_2].H_2O$ requires N, 45·50; Cu, 20·68 per cent}.

Use of caustic alkali solution in place of ammonia leads to partial decomposition and hence a more impure product. It seems ethylenedibiguanide is affected by strong alkalis.

### *Nickel Ethylenedibiguanidinium Salts*

*Sulphate* was prepared exactly in the same way as the corresponding complex sulphate of copper. It forms orange-yellow crystals, sparingly soluble in water. {Found: N, 33·90; Ni, 14·09; $SO_4$, 23·10. $[NiEn(BigH^+)_2]SO_4.2H_2O$ requires N, 33·52; Ni, 14·06; $SO_4$, 23·0 per cent}. (*cf.* also Dübsky and co-workers, *loc. cit.*).

*Chloride*.—The solution, obtained by extracting the fused mixture of ethylenediamine hydrochloride and dicyandiamide (see preparation of copper ethylenedibiguanidinium sulphate) after the removal of the unreacted dicyandiamide, was treated with a solution of nickel chloride and heated on the water-bath. The resulting orange-yellow solution, on cooling, deposited silky, orange-coloured needles of the complex chloride. This was recrystallised twice from water, washed and dried as usual. It decomposes on warming with dilute acids. {Found: N, 36·92; Ni, 15·35, Cl, 18·50. $[NiEn(BigH^+)_2]Cl_2.1\frac{1}{2}H_2O$ requires N, 36·31; Ni, 15·31; Cl, 18·49 per cent}. Magnetic susceptibility: $\chi_m = 0{\cdot}4436 \times 10^{-6}$.

*Equivalent conductivity at 34°.*

| $v$ (litres) | ... 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\Lambda_v$ = | ... 104 | 116 | 124 | 130 | 133 | 138 |

$\lambda\infty = 138·5$ (from Walden's formula).

Hence the equivalent mobility of $[Ni\ En(BigH^+)_2]$ at $34° = 138·5 - 87·78 = 50·72$, 87·78 being the mobility of Cl-ion at 34°. The corresponding value for $[Ni\ (BigH^+)_2]$, calculated from Rây and Purakayastha's results (*J. Indian Chem Soc.*, 1941, **18**, 219) = 54·6.

*Bromide* was obtained in the form of silky, orange needles by treating a strong solution of the complex chloride with that of potassium bromide. The product was purified by recrystallisation from hot water. {Found : Ni, 12·02 ; Br, 32·80. $[Ni\ En(BigH^+)_2]\ Br_2.2\frac{1}{2}H_2O$ requires Ni, 11·97 ; Br, 32·59 per cent}.

*Iodide* was prepared like the bromide from the complex chloride and potassium iodide. The orange-yellow, needle-shaped crystals were purified by recrystallisation from water. {Found: Ni, 10·42 ; I, 45·37. $[Ni\ En(BigH^+)_2]\ I_2.1\frac{1}{2}H_2O$ requires Ni, 10·36 ; I, 44·82 per cent}.

*Thiosulphate.*—Orange-yellow precipitate of the thiosulphate was at once obtained by adding a solution of sodium thiosulphate to that of the complx chloride. The substance is very sparingly soluble in water. {Found: $S_2O_3$, 50·75 ; Ni, 13·35 $[NiEn(BigH^+)_2]S_2O_3.2\frac{1}{2}H_2O$ requires $S_2O_3$, 50·57 ; Ni, 13·26 per cent}.

*Thiocyanate.*—When a concentrated solution of potassium thiocyanate was added to that of the complex chloride and cooled, silky orange-coloured crystals of the complex thiocyanate separated out. These were purified by recrystallisation. The product is moderately soluble in alcohol. {Found : S, 14·89 ; Ni, 13·66. $[Ni\ En(BigH^+)_2]\ (SCN)_2.1\frac{1}{2}H_2O$ requires S, 14·93 ; Ni, 13·70 per cent}.

*Nitrate* was obtained as a buff-coloured curdy precipitate from a solution of potassium nitrate and that of the complex chloride. The product was purified by recrystallisation from hot water. {Found : Ni, 13·48 ; $NO_3$, 28·80. $[Ni\ En(BigH^+)_2]\ (NO_3)_2\ 1\frac{1}{2}H_2O$ requires Ni, 13·44 ; $NO_3$, 28·39 per cent}.

*Nitrite.*—The light orange coloured curdy precipitate of the nitrite was obtained by adding a concentrated solution of sodium nitrite to that of the complex chloride. This was then recrystallised from water. {Found : N(total), 41·22; Ni, 14·59. $[NiEn(BigH^+)_2](NO_2)_2.1\frac{1}{2}H_2O$ requires N(total), 41·51 ; Ni, 14·50 per cent}.

When a solution of the complex chloride was treated with either dilute NaOH or ammonia, a silky, brownish orange precipitate of the complex base was obtained. This, on analysis, was found to contain proportionately more nitrogen and less nickel than the theoretically required value for nickel ethylenedibiguanidine or its hydroxide. All attempts to prepare a pure base, by altering the conditions of preparation, were unsuccessful (*cf.* preparation of the complex copper base).

## *Cobaltous Complexes*

*Cobaltous Ethylenedibiguanidinium Sulphate.*—A solution of ethylenedibiguanide sulphate (2 mol.) in dilute ammonia was added, drop by drop, with constant stirring to that of nickel-free

$CoCl_2, 6H_2O$ (1 mol.) in a little water. A greenish yellow silky precipitate separated at once. This turned yellow on warming on the water-bath. It was washed by decantation with cold water and then thoroughly on the filter until free from chloride and finally with alcohol. The product was dried over $CaCl_2$.

The compound is very sparingly soluble in water and is decomposed by dilute mineral acids, though comparatively stable towards dilute acetic acid. On treatment with dilute NaOH solution it changes into the corresponding light yellow complex base. On digestion with ammonia it undergoes gradual oxidation with the formation of cobaltic complexes giving a red solution. When treated with a solution of barium chloride an alkaline violet-coloured solution is produced, suggesting the formation of a hydroxo-aquo-cobaltic complex. A similar decomposition occurs with boiling water This is supported by the fact that the violet solution on treatment with sodium thiosulphate gives a green precipitate on acidification (*cf.* Rây and Ghosh, *J. Indian Chem. Soc.*, 1942, **19**, 1). {Found: N, 32·96; Co, 13·75; $SO_4$, 22·32. $[Co\,En(BigH^+)_2]SO_4{\cdot}2\tfrac{1}{2}H_2O$ requires N, 32·79 ; Co, 13·80 ; $SO_4$, 22·47 per cent}. It loses one molecule of water of hydration at 80°, but regains the same on subsequent exposure to the atmosphere.

*Cobaltous Ethylenedibiguanidinium Base*.—When the complex sulphate was treated with very dilute caustic soda solution in the cold, a light yellow precipitate of the free anhydro base was obtained in a rather impure state. This was washed first with ice-cold water and then with alcohol. The product was dried in vacuum over calcium chloride and lime. {Found: N, 47·8; Co, 21·10. $[Co\,En(Big)_2]$ requires N, 49·1 ; Co, 20·7 per cent}.

On shaking with dilute ammonia it undergoes oxidation to the cobaltic state giving a red solution. A similar oxidation occurs on boiling with water with the formation of cobaltous and cobaltic hydroxides.

*Cobaltous biguanidinium sulphate* was obtained as a greenish yellow silky precipitate by adding a cold solution of the calculated quantity (2 mols.) of simple biguanide sulphate in dilute ammonia to that of nickel-free $CoCl_2, 6H_2O$ (1 mol ). A solution of ammonium sulphate was then added to the mixture and the latter agitated for sometime in the cold. The precipitate was washed at first with ice-cold water containing a little ammonium sulphate, then with water alone and finally with cold alcohol. It was dried in vacuum over calcium chloride. Air should be excluded during washing and drying. {Found : N, 32·20; Co, 13·84; $SO_4$, 22·46; $H_2O$ (by loss at 105° in a current of nitrogen), 16·40. $[Co(BigH^+)_2]SO_4{\cdot}4H_2O$ requires N, 32·63; Co, 13·75; $SO_4$, 22·38; $H_2O$, 16·78 per cent}.

The anhydrous product is a pale dull yellow powder and gave on analysis, Co, 16·79%. (Calc. Co, 16·49%). On exposure to air at room temperature the dried product absorbed water to reform the original hydrated substance with $4H_2O$.

The substance is decompossd by warm water as already described (*vide supra*). In presence of ammonium sulphate solution it suffers slight oxidation forming a red solution of a cobaltic complex. When heated in air it forms an oxidised product with reddish brown colour.

*Cobaltous Biguanidine and its Hydroxide*.—The base was precipitated in the form of small silky yellow flakes when a solution of biguanide sulphate (2 mols.) in excess of caustic soda was added to that of nickel-free $CoCl_2, 6H_2O$ (1 mol.). The precipitate was washed first with ice-cold water, containing a few drops of ammonia. This was then filtered and washed on the filter successively with cold water, aqueous alcohol and finally with absolute alcohol. The filtration and washing were carried out in a current of hydrogen gas in Kapsenberg's automatic filtration apparatus. The product was dried in vacuum over concentrated $H_2SO_4$. In the dry state it is fairly stable and keeps pure for a long time. When moist, it undergoes slow oxidation in air with formation of red cobaltic *tris*biguanidinium hydroxide and separation of cobaltic oxide.

$$6[Co(BigH^+)_2]\,(OH)_2 + 3H_2O + 1\tfrac{1}{2}O_2 = 4[Co(BigH^+)_3](OH)_3 + 2Co(OH)_3$$

On boiling with water it changes slowly to give a violet solution of hydroxo-aquo-cobaltic *bis*biguanide complex, as it gives a green precipitate with sodium thiosulphate solution, when acidified. {Found : N, 48·10; Co, 20·60; $H_2O$(by loss at 70°), 12·26. $[Co(BigH^+)_2](OH)_2$ requises N, 47·50; Co, 20·45; $H_2O$, 12·21 per cent}.

The hydroxylic water is lost at 70° forming the anhydro-base. On analysis it gave: N, 52·15. $[Co(Big)_2]$ requires N, 54·06%. This indicates slight decomposition.

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# THE CHEMICAL EXAMINATION OF THE SEEDS OF *VATERIA INDICA*, PART II THE COMPONENT GLYCERIDES OF THE FAT

By C. Venkatarao and M. Narasingarao

The component glycerides of *Vateria indica* fat work out to be tri-stearin (2·5%), oleo-distearin (44·9%), oleo-palmitostearin (16·6%), oleo-dipalmitin (7·1%), dioleo-stearin (15·8%), dioleo-palmitin (13·0%) and triolein (0·2%).

The detailed examination of solid seed fats is at present of general theoretical as well as of practical importance. Theoretically there are two reasons: (*i*) to collect sufficient data to establish ultimately the limits within which specific mixture of fatty acids in seed fats is characteristic of particular botanical family and (*ii*) to obtain further evidence about their glyceride structure and about the even distribution of fatty acids throughout the whole glyceride molecule (Collin and Hilditch, *Biochem. J.*, 1929, **23**, 1273). The practical importance in the study of the glyceride structure of solid seed fats centres round their applicability in confectionery and soap industry in comparison with other favoured natural fats like Cacao butter, Borneo tallow and Kokum butter and hydrogenated fats. The physical properties namely the brittleness or 'snap' and low m.p. common to the above fats might be due to some similarities in glyceride structure.

The glyceride structure of the fat from *Vateria indica* was not investigated previously. The only other member of the family *Dipterocarpaceae*, which was completely studied with regard to its fatty acids and glyceride structure, is Borneo-tallow (Hilditch and Priestman, *J. Soc., Chem. Ind.*, 1930, **49**, 1977). A comparison of these fats with other solid seed fats is made at the end of this article. The glyceride composition was determined by methods recently adopted by a number of investigators (Amberger and Bauch, *Z. Unters. Nahr. Genussen*, 1924, **48**, 371; Hilditch and Lea, *J. Chem. Soc.*, 1927, 3106; Lewkowitsch., *J. Soc. Chem. Ind.*, 1933, **52**, 236 T; Hilditch and Ichaporia., *ibid.*, 1938, **57**, 44).

## EXPERIMENTAL

*Fully Saturated Glyceride.*—100 G of neutral fat (free acidity being removed by treating with excess of sodium carbonate solution) were oxidised repeatedly with powdered potassium permanganate in acetone medium according to Hilditch and Lea (*loc. cit.*), when 2·5 g. of neutral matter were obtained which contained 0·1 g. of non-saponifiable matter. The neutral substance on crystallising from ether gave pure tri-stearin, m.p. 71° (S.E. 294·7; I.V. 1·2). Hence the fat contains 2·4% of saturated glycerides mainly consisting of tri-stearin.

*Separation of the Glycerides from Acetone.*—300 G. of neutral fat were systematically crystallised from acetone at 0°. The least soluble glycerides (A) and soluble glycerides (B) were separated and the corresponding acids were liberated. These acids were esterified separately and subjected to fractional distillation.

* TABLE I

| | (A) | (B) | Neutral fat, |
|---|---|---|---|
| Wt. in g. | 198 | 102 | 300 |
| S.E. | 295·1 | 290·2 | 293·8 |
| I.V. | 28·5 | 51·1 | 36·1 |
| Glyceride by wt.% | 66 | 34 | 100 |
| Glyceride by mol % | 65·6 | 34·4 | 100 |

** TABLE II

| | Composition of acids by wt % | | | Composition by mol.% | | |
|---|---|---|---|---|---|---|
| | (A) | (B) | Mean | (A) | (B) | Mean |
| Palmitic | 7·798 | 25·36 | 13·7 | 8·56 | 27·27 | 14·97 |
| Stearic | 59·98 | 13·56 | 43·5 | 58·36 | 13·14 | 42·85 |
| Oleic | 33·18 | 61·58 | 42·5 | 33·07 | 59·61 | 42·17 |

* The percentage of fatty acids in each portion was determined in the usual way by identifying individual acids and calculating their proportions from the fractions.

** Myristic acid is taken together with palmitic acid and arachidic acid with stearic acid. Oleic acid contains traces of linoleic acid.

In order to find out the quantity of tri-$C_{18}$ glycerides in the fat, fractions (A) and (B) were fully hydrogenated with suspended nickel as catalyst until the iodine values were nearly nil: 1·2 and 2·1. The hydrogenated fat was systematically crystallised from ether at 0° when almost quantitative separation of tri-stearin was effected, 48·6% from (A) and 13·8% from (B) were obtained.

TABLE III

*Fractionation of the esters of solid acids at 2 mm. pressure*

| Fr. No | Temp. of fraction. | Weight. | S.E. | I.V. |
|---|---|---|---|---|
| 1 | 82-141° | 7·2 g. | 291·4 | 3·2 |
| 2 | 141° | 13·1 | 293·8 | 2·8 |
| 3 | 141°-145° | 9·7 | 295·2 | 2·6 |
| 4 | 145°-152° | 16·5 | 296·1 | 1·9 |
| 5 | 152°-154° | 8·4 | 299·2 | 2·1 |
| Residue | — | 11·6 | 300·2 | 1·9 |

From the above observations the glyceride composition of the fat is calculated and given in Table IV below.

TABLE IV

*Mol % of the fatty acids*

| | (A) | (B) | Total. |
|---|---|---|---|
| Mol % | 65·6 | 34·4 | 100 |
| Palmitic | 5·6 | 9·4 | 15·0 |
| Stearic | 38·3 | 4·5 | 42·8 |
| Oleic | 21·7 | 20·5 | 42·2 |

*Component glycerides (mol %)*

| | (A) | (B) | Total. |
|---|---|---|---|
| Tri-$C_{18}$ glycerides | 48·6 | 13·8 | 62·4 |
| (*a*) Fully saturated glycerides (tri-stearin) | 2·4 | — | 2·4 |
| (*b*) Mono oleo-disaturated glycerides | | | |
| Oleo-distearin | 44·1 | — | 44·1 |
| Oleo-palmitostearin | 16·8 | — | 16·8 |
| Oleo-dipalmitin | — | 7·5 | 7·5 |
| (*c*) Dioleo-mono-saturated glycerides | | | |
| Dioleo-stearin | 2·1 | 13·5 | 15·6 |
| Dioleo-palmitin | — | 13·2 | 13·8 |
| (*d*) Tri-unsaturated glycerides | | | |
| Triolein | — | 0·2 | 0·2 |

The following facts were taken into consideration in calculating the above proportions:

*Fraction A.*—The fully saturated glycerides, tristearin and oleo-distearin will remain in this fraction as they are most insoluble in acetone at 0°. Most of the oleo-palmitostearin being sparingly soluble in acetone at 0° will also be with this fraction.

*Fraction B.*—This fraction will consist mainly of di-unsaturated glycerides with small quantities of di-saturated glycerides. The whole of the tri-unsaturated glycerides will be found in this fraction only. But in the case of this fat no evidence has been found for its presence.

The fat from *Vateria indica* contains 2·5% of tri-stearin, 44·9% oleo-distearin, 16·6% oleo-palmitostearin, 15·8% dioleostearin; 13·0% dioleo-palmitin, 7·1% oleo-dipalmitin and 0·2% triolein.

| | Myristic % | Palmitic %. | Stearic %. | Arachidic%. | Oleic % | Linoleic %. | Association ratio in the total fatty acids. |
|---|---|---|---|---|---|---|---|
| *Vateria indica* | 0·7 | 13·0 | 43·1 | 0·4 | 42·5 | 0·1 | 1·34 |
| Borneo-tallow | 1·5 | 21·5 | 39·0 | — | 38·0 | — | 1·63 |

| | *Vateria indica* | Borneo-tallow* | Cacao butter† | Kokum butter‡ |
|---|---|---|---|---|
| M.p | 36-37° | 33-37° | 32-34° | 37-39° |
| Assn. ratio | 1·3 | 1·6 | 1·4 | 1·4 |
| Glycerides (in round figures) | | | | |
| Tri-stearin | 2·5 | 5 | 2 | 2 |
| Oleo-distearin | 45 | 40 | 19 | 59 |
| Oleo-palmitostearin | 16·5 | 31 | 52 | 14 |
| Oleo-dipalmitin | 7 | 8 | 6 | 2 |
| Stearo-diolein | 16 | 13 | 12 | 21 |
| Palmito-diolein | 13 | 3 | 9 | 2 |
| Triolein | — | — | — | 1 |

The fat from *Vateria indica* adds to the list of solid seed fats which follow the even distribution of fatty acids having association ratio on the total fatty acids 1·3 to 1·6.

The glyceride structure of the fat shows more similarities with that of Borneo-tallow.

It should find more favourable place in confectionery due to its pleasant smell and can be industrially utilised for soap-making and as a source of stearic acid.

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* Brishell and Hilditch, *J. Soc. Chem. Ind.*, 1938, **57**, 447.

† Collin, *J. Soc. Chem. Ind.*, 1929, **48**, 41 T.

‡ Vidyarthi and Dasa Rao, *J. Indian Chem. Soc.*, 1939, **16**, 437.

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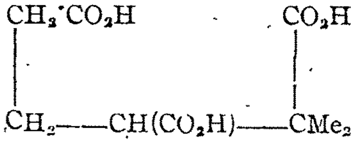
# STUDIES IN THE REARRANGEMENT OF CAMPHORQUINONE. PART I. FORMATION AND REACTIONS OF THE INACTIVE MODIFICATION OF 2 : 2 : 3-TRIMETHYL*CYCLO*HEXAN-4-ONE-1-CARBOXYLIC ACID

By Ram Narayan Chakravarti

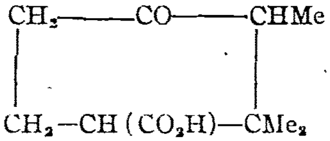
Following the work of Samuel and Manasse (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831), synthetic camphor has been converted into the racemic modification of 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid. The keto-acid on Clemmensen reduction furnishes 1 : 2 : 2-trimethyl*cyclo*hexane-3-carboxylic acid. The methyl ester of the latter on dehydrogenation with selenium affords *o*-xylene and 1 : 2-dimethylbenzene-3-carboxylic acid, which is in accord with Simonsen's formula (*J. Chem. Soc.*, 1927, 77) for the keto acid. A partial synthesis of the keto-acid is also described.

In the course of their classical researches on the action of sulphuric acid on camphorquinone, Manasse and Samuel (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831) isolated a dextro-rotatory acid, $C_{10}H_{16}O_3$, m.p. 97-98°, which was believed to be a γ- or a δ-ketonic acid. On oxidation with nitric acid (Gibson and Simonsen, *J. Chem. Soc.*, 1925, **127**, 1295), however, the keto-acid yielded β-methylpentane-βγε-tricarboxylic acid (I) in an excellent yield. It followed, therefore, that the keto-acid could be best represented by the two alternative structures (II) and (III).

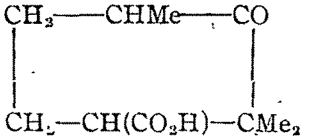


$$\begin{array}{lcr} CH_2\cdot CO_2H & & CO_2H \\ | & & | \\ CH_2 & \text{——}CH(CO_2H)\text{——} & CMe_2 \end{array}$$

(I)

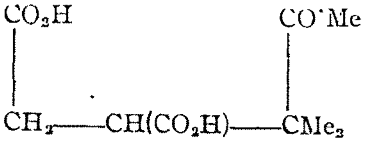


(II)



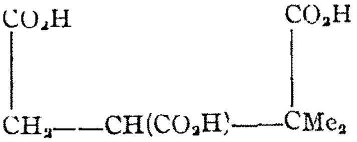
(III)

Subsequently, it was found by Bhagvat and Simonsen (*J. Chem. Soc.*, 1927, 77; *cf.* Bredt-Savelsberg, Zaubrecher and Knieke, *Ber.*, 1927, **60**, 1801) that the keto-ester on bromination yielded two stereoisomeric dibromo-esters, $C_{11}H_{16}O_3Br_2$, which on treatment with alkali gave a diketo-acid, $C_{10}H_{14}O_4$. This suggested that the dibromo-ester had two bromine atoms attached to the same carbon atom—a fact most simply explained if the original keto-acid had formula (II). In conformity with this view there is the fact that the diketo-acid behaves like an 1:2-diketone and on treatment with alkali passes into a hydroxy dibasic acid, $C_{10}H_{16}O_5$. The latter on dehydration, followed by oxidation, gave successively γ-acetyl-γγ-dimethylpropane-αβ-di-carboxylic acid (IV) and αα-dimethyl tricarballylic acid (V).



$$\begin{array}{lcr} CO_2H & & CO\cdot Me \\ | & & | \\ CH_2 & \text{——}CH(CO_2H)\text{——} & CMe_2 \end{array}$$

(IV)



$$\begin{array}{lcr} CO_2H & & CO_2H \\ | & & | \\ CH_2 & \text{——}CH(CO_2H)\text{——} & CMe_2 \end{array}$$

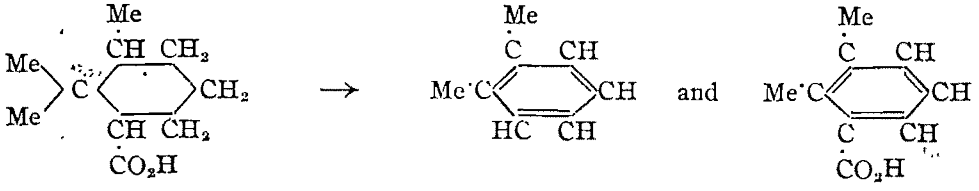
(V)

The foregoing results appear to establish definitely that the keto-acid, first described by Manasse and Samuel, must be *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid (II). Unfortunately, no direct proof is available regarding the prsence of a keto-methylene group in it. (*cf.* Bhagvat and Simonsen, *loc. cit.*, p. 81).

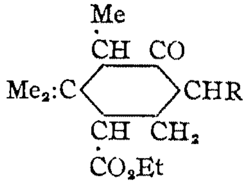
The formation of a keto-acid (II) from camphorquinone is somewhat remarkable. According to Ingold (*Chem. Soc., Ann. Report*, 1927, 122) a change related to the Wagner rearrangement takes place through the intervention of a molecule of water whereby one of the *cyclo*pentane rings of camphorquinone undergoes fission and the other simultaneously enlarged. This facile rearrangement, which takes place even when camphorquinone is brominated (Manasse and Samuel, *loc. cit.* Evans, Simonsen, and Bhagvat, *J. Chem. Soc.*, 1934, 444), possesses more than an ordinary interest and it seemed desirable to undertake the synthesis of the keto-acid in order to establish its constitution definitely.

As has been stated by Gibson and Simonsen (*loc cit.*) it is a matter of some difficulty to obtain an optically pure specimen of the keto-acid since the latter possesses two centres of asymmetry one of which is expected to suffer racemisation more readily than the other. It was necessary, therefore, to prepare the hitherto unknown racemic modification of the keto-acid, which would serve as a reference compound for purposes of direct comparison.

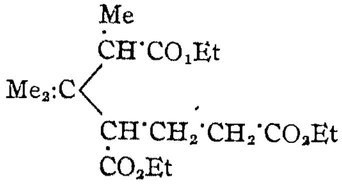
In the first instance synthetic camphor has been converted into the corresponding quinone by oxidation with selenium dioxide (Simonsen, Evans and Ridgion, *J. Chem. Soc.*, 1934, 137). The latter on treatment with cold concentrated sulphuric acid according to the method of Manasse and Samuel (*loc. cit.*) gives the racemic modification of the keto-acid, $C_{10}H_{16}O_3$, m.p. 109°, which has been further characterised by the preparation of a semicarbazone, m.p. 230°. The methyl ester is, however, obtained as an oil, b.p. 100°/4mm., and thus differs from the methyl ester of the corresponding dextro-acid which is a crystalline solid, m.p. 82-83°. The new keto-acid on Clemmensen reduction furnishes a liquid acid, b.p. 118°/5 mm., which readily forms a crystalline *p*-phenylphenacyl ester, m.p. 114°. On the basis of Simonsen's formula for Manasse and Samuel's keto-acid, the above liquid acid should be represented as 1 : 2 : 2-trimethyl*cyclo*hexane-3-carboxylic acid (VI). As an additional control on the constitution of this acid its methyl ester has been dehydrogenated with selenium at 340° in a closed tube for 28 hours. The resulting product on hydrolysis yields a neutral liquid, which is found to be *o*-xylene by its boiling point and by its oxidation to phthalic acid. The alkaline solution on acidification furnishes an acid which was readily identified as 1:2-dimethylbenzene-3-carboxylic acid (*cf.* Jacobson, *Ber.*, 1898, **19**, 2518) by its m.p. 144°, and by analysis.



(VI)



(VII)



(VIII)

As has been mentioned already, Simonsen and his co-workers (*loc. cit*) were unable to obtain direct evidence regarding the presence of a -$CH_2$ CO- grouping in the keto-acid (II). It has now been found, however, that the ethyl ester (VII, R=H) of the keto-acid readily enters into combination with ethyl oxalate leading to the formation of the oxalyl derivative (VII, R=CO·$CO_2Et$) which on distillation under reduced pressure gives up carbon monoxide with the production of ethyl 2:3:3 trimethyl*cyclo*hexan-1-one-4:6-dicarboxylate (VII, R=$CO_2Et$) in an excellent yield.

The latter shows all the properties of a β-ketonic ester and on hydrolysis with hydrochloric acid affords the keto-acid (II) Curiously enough the same product is also obtained when the keto-ester (VII, R=$CO_2Et$) is heated with moderately concentrated alcoholic potash. This is precisely analogous to the behaviour of ethylcamphor carboxylate (*cf.* Haller and Minguin, *Compt. rend.*, **110**, 400, Ruzicka and Kuhn, *Helv. Chim. Acta*, 1920, **3**, 748). On digestion with sodium ethoxide in a sealed tube at 150-200° for 24 hours, however, the ester (VII, R=$CO_2Et$) is mainly converted into the triethyl ester (VIII), b.p 160°/4mm. The latter on hydrolysis yields the corresponding tricarboxylic acid as a resin which unfortunately could not be induced to crystallise. The triethyl ester (VIII), however, behaves normally with sodium yielding the keto-ester (VII,R=$CO_2Et$) which on hydrolysis in the usual way leads to the formation of the keto-acid (II). This constitutes, therefore, a partial synthesis of Manasse and Samuel's keto-acid. The synthesis of the triethyl ester will form the subject of a later communication.

## EXPERIMENTAL

### *Preparation of* dl-*Modification of* 2:2:3-*Trimethyl*cyclo*hexan-4-one-1-carboxylic Acid*

dl-*Camphorquinone*.—A mixture of *dl*-camphor (30 g.), selenium dioxide (36 g.), and acetic anhydride (30 c.c.) was heated in an oil-bath at 140-150° for 3 to 4 hours. It was then cooled and filtered, the residue of selenium being washed with acetic acid. The orange-yellow acetic acid solution was partially neutralised with aqueous potassium hydroxide when a curdy yellow precipitate of *dl*-camphorquinone was obtained along with a little unchanged camphor. After one crystallisation from dilute alcohol it was obtained as a yellow powder, m.p. 192°, and was sufficiently pure for the next operation.

*Action of cold concentrated sulphuric acid on* dl-*Camphorquinone: Formation of* dl-2:2:3-*Trimethyl*cyclo*hexan-4-one-1-carboxylic Acid* (II).—Dry, finely powdered *dl*-camphorquinone (10 g.) was added gradually during half an hour to concentrated sulphuric acid (83 c.c.), cooled in ice and stirred mechanically. The stirring was continued for another 45 minutes when a clear solution was obtained. It was then poured on to crushed ice with stirring. The solution was saturated with salt and extracted repeatedly with ether. The keto-acid was separated from neutral impurities by extracting the ethereal solution with 10% sodium carbonate solution. The alkaline solution was acidified, saturated with salt, and extracted with ether. dl-2:2:3-*Trimethyl*cyclo*hexan-4-one-1-carboxylic acid* (8 g.) was obtained as a crystalline solid on evaporation of the ether.

The *semicarbazone* was readily obtained on heating a solution of the keto-acid in a little alcohol with aqueous semicarbazide acetate solution. It crystallises from a large volume of spirit as a sandy white powder*, which decomposes at 230°. (Found: C, 54·4; H, 8·1. $C_{11}H_{19}O_3N_3$ requires C, 54·7; H, 7·9 per cent).

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* Mixed melting point of this with the semicarbazone of the dextro-acid is 229°.

The *pure* keto-acid was obtained by warming the semicarbazone with 15% hydrochloric acid till a clear solution was obtained It was then cooled saturated with salt and extracted with ether. The solid residue obtained on evaporation of the ether was crystallised from water when dl-2 : 2 : 3-*trimethyl*cyclo*hexan-4-one-1-carboxylic acid* (II) was obtained in colourless needle-shaped crystals,* m p 73-74° and containing one molecule of water of crystallisation. (Found : $H_2O$, 8·9. $C_{10}H_{16}O_3 \cdot H_2O$ requires $H_2O$, 8·9 per cent).

The hydrated acid readily loses water when kept in a desiccator or heated. The *anhydrous* acid, thus obtained, crystallises from light petrol in transparent plates melting at 109°. Unlike the corresponding active acid it is not hygroscopic. (Found : C, 65·4 ; H, 8·7. $C_{10}H_{16}O_3$ requires C, 65·2 ; H, 8 7 per cent).

The *methyl ester* was prepared by heating the dry keto-acid (2 g.) on a water-bath for 6 hours with absolute methyl alcohol (20 c.c.) and 2 c.c. methyl alcoholic hydrogen chloride. The alcohol was then distilled off. The residue was taken up in ether and washed with dilute sodium carbonate solution and water. The ether was evaporated and the liquid remaining distilled in *vacuo*, b.p. 100°/4mm., yield, 2g. Its active isomer is a solid, m.p. 82-83°. (Found : C, 66·4 ; H, 9·00. $C_{11}H_{18}O_3$ requires C, 66·6 ; H, 9·09 per cent).

The *ethyl ester* (VII, R=H) was prepared by heating the acid (14 g.) on a water-bath for 8 hours with absolute alcohol (80 c.c.) and 8 c.c. of alcoholic hydrogen chloride (saturated at 0°), and working up in a similar manner. It is a liquid boiling at 120°/6 mm., yield 12·5 g. (Found : C, 67·8 ; H, 9 4. $C_{12}H_{20}O_3$ requires C, 67·9 ; H, 9·4 per cent).

### *Degradation of the Keto-acid,* $C_{10}H_{16}O_3$, *to* o-*Xylene and* 1 : 2-*Dimethylbenzene-3-carboxylic Acid*

1 : 2 : 2-*Trimethyl*cyclo*hexane-3-carboxylic Acid* (VI).—The keto acid (5·1 g.) was heated on a sand bath for 6 hours with concentrated hydrochloric acid (45 c c.) and granulated zinc (60 g.), previously amalgamated with a 5% solution of mercuric chloride. More hydrochloric acid (60 c.c.) was then added and the refluxing was continued for 12 hours more. When cold it was extracted with ether. The extract was washed with water and ether evaporated. The liquid remaining was finally distilled in *vacuo*. It was obtained as a colourless liquid (3 1 g.), boiling at 118°/5 mm. (Found : C, 70·2 ; H, 10 5. $C_{10}H_{18}O_2$ requires C, 70·6 ; H, 10·6 per cent).

The p-*phenylphenacyl ester* crystallises from ethyl alcohol in colourless needles, m.p. 114°. (Found : C, 79·1 ; H, 7·7. $C_{24}H_{28}O_3$ requires C, 79·1 ; H, 7·7 per cent).

The *methyl ester* was prepared by refluxing the above acid (4·9 g.) on the water-bath for 8 hours with absolute methyl alcohol (25 c.c ) and concentrated sulphuric acid (1·3 c.c.). When cold it was diluted with water and the separated oil taken up in ether. The extract was washed with dilute sodium carbonate solution and water, and the solvent evaporated after drying over anhydrous calcium chloride. The residual oil on distillation gave a colourless liquid boiling at 95°/12 mm., yield, 4·5 g. (Found : C, 71·6 ; H, 10·8. $C_{11}H_{20}O_2$ requires C, 71·7 ; H, 10·8 per cent).

*Selenium Dehydrogenation of Methyl 1 : 2 : 2-Trimethyl*cyclo*hexane-3-carboxylate : Formation of* o-*Xylene and 1 : 2-Dimethylbenzene-3-carboxylic Acid.*—A mixture of the methyl ester (4·39 g.) and selenium (7·3 g.) was heated at 340° in a sealed tube for 28 hours. The product was then taken up in ether and filtered. The clear ethereal filtrate was washed with dilute sodium carbonate solution (A), and water, and dried over anhydrous calcium chloride. It was carefully fractionated using a short but efficient fractionating column. After the evaporation of the ether, the temperature rose up rapidly to 140° and a liquid hydrocarbon (1·5 g.) was obtained boiling constantly at this temperature.

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* Mixed melting point of this acid with the hydrated dextro-acid is 62°

The hydrocarbon, thus obtained, was heated on the water-bath with water (175 c.c.), and finely powdered potassium permanganate (9 g.) was added in small amounts, the mixture being well shaken from time to time. After the oxidation was complete, excess of permanganate was decomposed with a few drops of methyl alcohol. It was then filtered and the filtrate concentrated, acidified and extracted with ether. On removal of the solvent phthalic acid (1 g.) was obtained. It gave phthalic anhydride on heating, m.p. 131° (mixed m.p. responds to fluorescein test and forms the aniline salt, m.p. 157°).

The sodium carbonate extract (A), on acidification, gave a solid acid (0·6 g.) almost insoluble in cold water. It crystallises from dilute alcohol, m.p. 144° and was found to be 1 : 2-dimethylbenzene-3-carboxylic acid. (Found : C, 72·2 ; H, 6·8 ; Eqiv., 150·9. $C_9H_{10}O_2$ requires 72·0 ; H, 6·7 per cent. Eqiv., 150).

### *A partial Synthesis of the Keto-acid of Manasse and Samuel*

*Ethyl* 2 : 3 : 3-*Trimethyl*cyclo*hexan*-1-*one*-4 6-*dicarboxylate* ( VII, R = $CO_2Et$ ).—A mixture of ethyl 2 : 3 : 3-trimethyl*cyclo*hexan-1-one 4-carboxylate (11·5 g ) and diethyl oxalate (7·9 g.) was added very slowly with shaking to a solution of sodium (1·25 g.) in absolute alcohol (16·5 c.c.) cooled in a freezing mixture, and kept overnight. It was then treated with ice-water and extracted with ether to remove any neutral matter present. The alkaline solution was acidified with ice-cold dilute sulphuric acid and extracted with ether. The extract was well washed with water, dried and the ether evaporated. The residual oil was heated to 110-120° under reduced pressure for about an hour and then under atmospheric pressure for 3-4 hours till the evolution of carbon monoxide ceased, the temperature during this period being gradually raised from 160° to 200°. It was finally distilled in *vacuo* when the product was obtained as a colourless oil, b.p. 155°/6 mm., yield 9·9 g. It gave a deep violet colouration with alcoholic ferric chloride. ( Found : C, 62·8 ; H, 8·3. $C_{15}H_{24}O_5$ requires C, 63·3 ; H, 8·4 per cent).

*Ethyl αββ-Trimethylpentane-αγε-tricarboxylate* (VIII).—The above keto-dicarboxylic ester (5 g.) was heated in a closed tube at 150-200° for 24 hours with a solution of sodium (0·41 g.) in absolute alcohol (24 c.c.). The alcohol was then distilled off under reduced pressure. It was then treated with water and extracted with ether. The residue obtained on evaporation of the ether was fractionated in *vacuo*. At first some low boiling product distilled off and then the temperature rose to 160°/4mm. and about 2·3 g. of *ethyl αββ-trimethylpentane-αγε-tricarbxoylate* was obtained. It gave no colouration with alcoholic ferric chloride. (Found C, 61·5 ; H, 9·0. $C_{17}H_{30}O_6$ requires C, 61·8 ; H, 9·1 per cent).

The *free acid* was obtained as a gum by hydrolysing the above triethyl ester with aqueous alcoholic potash.

*Sodium Condensation of Ethyl αββ-Trimethylpentane-αγε-tricarboxylate* (VIII) : *Formation of Ethyl* 2 : 3 : 3-*Trimethyl*cyclo*hexan*-1-*one*-4 . 6-*dicarboxylate* (VII, R = $CO_2Et$).—The tricarboxylic ester (5 g.), obtained above, was heated on the water-bath with a fine suspension of sodium (0·5 g.) in benzene (12 c.c.) When whole of the sodium went into solution, it was treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed and the benzene evaporated. The residual oil on distillation gave the product (2·5 g.), b.p. 150°/5 mm, *dl*-2 : 2 : 3-*Trimethylcyclohexan-4-one-1-carboxylic Acid* (II).—For the hydrolysis of the above keto-ester, concentrated alcoholic potassium hydroxide was found to be better than dilute hydrochloric acid. The keto-ester (2 g.) was heated on the water-bath for 3 hours with potassium hydroxide (3 g.) in 20% aqueous alcoholic solution. The alcohol was then evaporated off with the addition of water. The alkaline solution was acidified, saturated with salt and extracted with ether. The residue obtained on evaporation of the ether was directly converted into the *semicarbazone*. It crystallised from a large volume of alcohol as a sandy white powder, m.p. 230-31° and there was no depression of the melting point on mixing it with the semicarbazone of the keto-acid as obtained directly from camphorquine. (Found :. C, 54·6 ; H, 7·9. $C_{11}H_{19}O_3N_3$ requires. C, 54·7 ; H, 7·9 per cent).

The *pure* acid was obtained by hydrolysing the semicarbazone with dilute hydrochloric acid by warming on the water-bath till a clear solution was obtained It was then saturated with salt and extracted with ether. On evaporation of the ether a solid residue was obtained which on crystallisation from water melted at 72-73°. On drying in a desiccator it melted at 109°. Moreover, there was no depression of the melting point when the latter was mixed with the *anhydrous* sample of *dl*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid. (Found : C, 65·0 ; H, 8·5. $C_{10}H_{16}O_3$ requires C, 65·2 ; H, 8 6 per cent).

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# SOME REACTIONS OF CARBOXYLIC ACIDS IN AQUEOUS SOLUTION

By P. S. MacMahon and T. N. Srivastava

The phenomenon of so-called " activation " of oxalic acid by the addition of $KMnO_4$ in deficiency in aqueous solution is not shown by other polycarboxylic acids. Enhanced reducing power towards certain metallic salts, such as mercuric chloride and gold chloride (chloroauric acid) thereby acquired, has hitherto been erroneously regarded as being the result of a process of chemical induction. The experimental results can be explained, however, by the formation of intermediate oxidation products of varying degrees of stability; in general, oxy-carboxylic acids which strongly reduce certain metallic salts. The reactions are stoichiometric in nature and thus have nothing in common with the permanganate-oxalate-mercuric chloride reaction.

The reaction between oxalic acid and gold chloride is exceptional, in as much as it is strongly retarded both in light and in the dark by oxygen.

So called photochemical after-effects, in those cases in which they have actually been confirmed, are also due to the presence of definite stable products formed in the photoreaction with halogens.

The present investigation was prompted by the results observed in the permanganate-oxalate-mercuric chloride reaction; it was thought desirable to examine more closely how other simple polycarboxylic acids reacted to similar treatment with permanganate and whether they became "activated" thereby *i.e.* their power of reducing certain metallic salts was enhanced. Moreover, some of these acids, in particular citric, malic and tartaric, have been stated to exhibit the phenomenon of photochemical after-effect when halogenated in light, in a manner similar to the reaction between iodine and oxalate, but no general mechanism has been suggested to account for the observed results.

These reactions have been studied by Dhar (*J. Chem. Soc.*, 1917, **111**, 699) who found that the addition of $KMnO_4$ promoted reaction with $HgCl_2$ and thus regarded them as examples of chemical induction, where $KMnO_4$ was supposed to act as an inductor. The experiments were carried out at 100° and the extent of reaction measured by the weight of calomel precipitated. At this temperature, however, it is well known that tartaric, malic, malonic and citric acids are all oxidised, among other products, to formic acid, which reduces $HgCl_2$ quantitatively. They cannot therefore be regarded as induced reactions.

We find that at room temperature (about 20° to 25°) a very slow reduction takes place in the dark (it must not be overlooked that mixtures of these acids and $HgCl_2$ are photosensitive to diffused light) on addition of $KMnO_4$ to the aqueous solutions. All the acid mixtures examined produced calomel, except citric acid, in the case of which the precipitate does not contain calomel in appreciable amounts but consists of a complex insoluble substance which yields on washing with hot water both Cl and a carboxylate. At 100° the precipitate is exclusively calomel.

We have been able to show experimentally that at room temperature acetone dicarboxylic acid, formed as an intermediate product by the action of $KMnO_4$ on citric acid, reacts slowly in solution with $HgCl_2$, forming a similar complex substance. A similar reaction between citric acid and $HgSO_4$ has already been described by Deniges (*Compt. rend.*, 1899, **128**, 680) producing the complex $Hg_3O_2SO_4.2[(CH_2)_2CO(CO_2)]Hg$. It is clear that the reactions of these carboxylic acids treated with $KMnO_4$ are of a different character to the phenomena associated with the so-called *activation* of oxalic acid, and that the activity observed with the former is due to the presence of reactive oxidation products.

In view of the unsuitability of $HgCl_2$ as a reagent, owing to the possibility of formation of complexes, a further series of experiments was carried out, using gold chloride in its place.

Reduction of gold chloride by organic acids with and without the addition of $KMnO_4$ has also been studied by Dhar (*loc. cit.*), who found a considerable enhancement of the rate of reaction to take place. These were also considered to be induced reactions by the author.

It was soon evident, however, that these cannot be induced reactions, since we found that the same reducing power was retained in solutions after all the permanganate had been used up *i.e.* reduced to the $Mn^{II}$ state. This again suggested the presence of intermediate oxidation products formed by the action of permanganate on the acids under investigation, and such has actually proved to be the case. It must also be emphasised that the reactions between the pure acids and gold chloride are highly sensitive to the diffused light of the laboratory, so that comparable results can only be obtained in the dark.

## EXPERIMENTAL

The analytically pure acids employed were recrystallised from conductivity water.

5 C.c. of the $N/10$ acids (except in the case of malonic acid where the concentration was 0·4 $N$) were treated with 0·5 c.c. of $N/10$-$KMnO_4$ and 2 c.c. gold chloride (as $HAuCl_4$) containing 1·8 g. Au per litre, were added at known intervals to the mixture, the whole being made up to 25 c.c. The experiments were carried out at room temperature (about 20°) except in the case of malonic acid, where the reaction was very slow, and the temperature in consequence had to be raised to 30°.

In some of the experiments carried out in an atmosphere of nitrogen, the same apparatus was employed as that mentioned in a previous communication (MacMahon and Lal, *J. Indian Chem. Soc.*, 1943, **20**, 143), the time required for the reduction of gold chloride being noted after mixing the reagents in the sealed reaction vessel. Oxalic, citric, malic, tartaric and malonic acids were investigated in this manner.

*Effect of Light.*—Other things being equal, Table I shows the order of sensitivity in light and comparative rate of reaction in the dark of equivalent concentrations of the above mentioned acids in reducing gold chloride. The figures show the time taken in *minutes* for an arbitrarily selected depth of colour of reduced gold to appear.

TABLE I

| | Oxalic. | Citric. | Malic. | Tartaric. | Malonic. |
|---|---|---|---|---|---|
| Sunlight | 2 | 3½ | 4½ | 10 | 35 |
| Diffused light | 8 | 30 | 50 | 120 | 40 |
| Dark | 20 | 160 | 5 hrs.<br>(approx.) | 2 days<br>(approx.) | 39 |

TABLE II

| | Oxalic. | Citric | Malic. | Tartaric. | Malonic. |
|---|---|---|---|---|---|
| Air | 8 | 29 | 50 | 110 | 43 |
| Nitrogen | ½ | 60 | 105 | 210-220 | 85 |

Table I reveals that there is practically no photochemical acceleration in the case of malonic acid. Pre-illumination of the reactants separately does not produce any effect on the time of reduction.

*Effect of Atmospheric Oxygen.*—Table II shows that in diffused light the reaction is largely retarded by oxygen in the case of oxalic acid, while in the case of the other acids it is somewhat accelerated. If these reactions are carried out in the dark under nitrogen, they are not affected by oxygen, except oxalic acid, where retardation is also observed.

Thus 5 c.c. of *N*/10-oxalic acid and 2 c.c. of gold chloride made up to 25 c.c. gave the following results in the dark.

TABLE III

| Temp. | Time for reduction<br>in air | <br>under nitrogen. |
|---|---|---|
| 3° | 70 min. | 15 |
| 20° | 20 | ½ |
| 35° | 2½ | Immediate |

*Effect of Temperature and Concentration of Acid.*—Increase of temperature and concentration, as is to be expected, increases the rate of reduction, but the relative values remain unchanged as given in Table I and figures are therefore not given.

*Effect of Addition of* KCl *or* NaCl.—The effect of addition of these salts is to stabilise gold chloride by the formation of a co-ordination complex (Lenher, *J. Amer. Chem. Soc.*, 1913, **35**, 546) and the rate of reduction is thus proportionately decreased. With large excess of the salts the photoreaction in diffused light is suppressed.

*Hydrogen Peroxide.*—It has been stated by Sonstadt (*Chem. News*, 1898, **77**, 74) that hydrogen peroxide is produced in small amounts when gold chloride is reduced in aqueous solution. By reducing the latter with carboxylic acids and removing the colloidal gold by shaking with freshly precipitated aluminium hydroxide in the cold and filtering, we have not been able to confirm the presence of $H_2O_2$ in the filtrates. Traces of $H_2O_2$ in aqueous solution are not removed by aluminium hydroxide.

*Effect of* $KMnO_4$.—The reaction between gold chloride and the carboxylic acids is accelerated by the addition of small quantities of $KMnO_4$, but when the gold chloride is added to the mixture, immediately after the latter has been completely reduced, the rate of reaction is found to be at its maximum.

TABLE IV

| | Oxalic. | Citric. | Malic. | Tartaric. | Malonic. |
|---|---|---|---|---|---|
| Without $KMnO_4$ | 8 min. | 30 min. | 50 min. | 120 min. | 40 min. |
| $KMnO_4$ added together with $AuCl_3$ | 9* | 8 | 40 | 80 | 32 |
| $AuCl_3$ added after the decolourisation of $KMnO_4$ | 5 | ½ | 8 | 30 | 20 |

*Oxalic acid is an exception.

By increasing the quantity of $KMnO_4$, the rate of reaction is still further increased.

TABLE V

| | Oxalic. | Citric. | Malic. | Tartaric. | Malonic. |
|---|---|---|---|---|---|
| 0·5 C.c. of $KMnO_4$ (*N*/10) decolourised | 5 (0·1 c.c. $KMnO_4$) | ⅓ | 8 | 30 | 20 |
| 0·75 C.c. of $KMnO_4$ (*N*/10) decolourised | 4 15 (0·2 c.c. $KMnO_4$) | ¼ | 6½ | 25 | 16 |

It is clear from these tables that $KMnO_4$ is not an inductor, but that the reaction must be due to the formation of oxidation products highly reactive towards gold salts. The effect of possible oxidation products such as $H_2O_2$, aldehydes, acetone and formic acid, as well as $Mn^{II}$ ions, added in amounts corresponding to the concentration of $KMnO_4$ employed, were all found to be negligible.

*Change of Reducing Power of the Decolourised Solutions* ($KMnO_4$ *and carboxylic acid*) *with Time.*—Gold chloride was added to the aqueous solutions of the acids, previously oxidised with $KMnO_4$, at varying intervals of time.

TABLE VI

| | Citric. | Malic. | Tartaric | Malonic |
|---|---|---|---|---|
| Immediately | ½ | 8 | 30 | 20 |
| After 1 day | 1·20 | 14 | 45 | 30 (after 15 min.) |
| After 2 days | 2·15 | 16 | 50 | 38 (after 30 min ) |
| After 3 ,, | 3·20 | 18 | 54 | |
| After 4 ,, | 4·05 | 19 | 60 | |
| After 5 ,, | 5·30 | 20 | — | |
| After 8 ,, | 6·30 | 23 | 80 | |
| After 14 ,, | 20 | 41 | — | |

It is well known that all these organic acids, except oxalic, are ultimately oxidised to formic acid by $KMnO_4$, but the above behaviour suggests that when there is a deficiency of the latter, intermediate oxidation products of varying degrees of stability are formed which reduce gold chloride rapidly.

*Citric Acid.*—Kuyper (*J. Amer. Chem. Soc.*, 1933, **55**, 1722) suggested that citric acid was oxidised by $KMnO_4$ to formic acid with the intermediate formation of acetone dicarboxylic acid.

We have prepared this acid by the method of Pechmann (*Annalen*, 1899, **261**, 156), and found that 5 mg. of the crystals dissolved in 25 c.c. of water reduced gold chloride instantly. Its presence in solutions of citric acid to which $KMnO_4$ has been added has been shown by adding bromine water, when a precipitate appears which has been identified as pentabromoacetone.

$$(CH_2)\ CO\ (COOH)_2 + 5\ Br_2 = 2CO_2 + 5HBr + C_2HBr_5CO.$$

Moreover, by adding quantities of the acid, corresponding to the $KMnO_4$ reduced in the above experiments, to solutions of citric acid and $Mn^{II}$ ions in corresponding concentration, it has been found possible to reproduce exactly the behaviour of citric acid in Table VI.

In aqueous solution the acid decomposes on long keeping to $CO_2$ and acetone. The results indicate that acetone dicarboxylic acid persists in solution down to vanishingly small concentrations for 14 days or more at 20°.

*Malic Acid.*—Deniges (*Compt. rend.*, 1900, **130**, 32) suggested that malic acid was oxidised to formic acid by $KMnO_4$ with intermediate formation of oxalacetic acid [HOOC.CH=C(OH)·COOH] but this has been questioned by Hatcher and West (*Trans. Roy. Soc.*, 1927, **21**, 269).

We have prepared oxalacetic acid by the method of Fenton and Jones (*J. Chem. Soc.*, 1900, **77**, 77), by the action of $H_2O_2$ on malic acid in presence of $FeSO_4$. This acid has also been found to reduce gold chloride immediately, but when added to solutions of malic acid and $Mn^{II}$ in the same proportions as above, the same rate of loss of reducing power was not observed. The activity disappeared much more rapidly than in solutions of malic acid treated with $KMnO_4$, suggesting that an intermediate oxidation product stabler than oxalacetic acid is present and not yet successfully identified.

*Tartaric Acid.*—Fenton (*J. Chem. Soc.*, 1894, **65**, 899) states that when tartaric acid solutions are treated with $KMnO_4$ in the presence of small quantities of iron, dioxymaleic acid [$HO_2C(COH) : C(OH).COOH$] is formed.

We have prepared this acid by Fenton's method and it has also been found to reduce gold chloride very rapidly. It decomposes slowly in aqueous solutions at room temperature to $CO_2$ and glycol aldehyde (Fenton, *ibid*, 1896, **69**, 546). When added to a mixture of tartaric acid and $Mn^{II}$ ions in small quantities (0·5 mg.), approximately the same rate of loss of reducing power as that observed with $KMnO_4$-treated tartaric acid can be reproduced. The corresponding results for these three acids (Table VII) may be compared with Table VI.

TABLE VII

| | | Days | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Acid. | Immediately. | 1 | 2 | 3 | 4 | 6 | 8 | 14 |
| Acetone dicarboxylic | 40 sec. | 1·45 | 2·45 | 3·30 | 4 15 | 6·00 | 7·00 | 18·00 |
| Oxalacetic | 6 | 10 | 13 | 25 | 38 | 44 | Slow | |
| Dioxymaleic | 27 | 45 | 48 | 53 | 61 | — | 75 | |

The formation of dioxymaleic acid by $KMnO_4$ has, however, been disputed by Hatcher and West (*Trans. Roy. Soc.*, 1926, **20**, 327) so that the question of the identity of the acid must remain open at present.

*Malonic Acid.*—The intermediate oxidation product in this case is very unstable and disappears within half an hour, so that its identification has not yet been found possible.

*Oxalic Acid.*—The behaviour of this acid is unique, as we have shown the reaction with gold chloride to be inhibited by atmospheric oxygen both in light and in the dark.

Addition of $KMnO_4$ slightly accelerates the reduction of gold chloride when the latter is added to the nearly decolourised mixture in air. This is to be expected on account of the presence at this stage of the highly reactive $Mn(C_2O_4)_2$ ion (MacMahon and Lal, *loc. cit.*) Further investigations are proceeding.

*Photochemical "after-effects".*—So-called after-effects have been stated to follow the photobromination of citric, malic and tartaric acids (Dhar, *J. Indian Chem. Soc.*, 1925, **2**, 277).

We have confirmed them in the cases of citric and tartaric acids only. Pure recrystallised malic acid and bromine react rapidly in sunlight but show no after-effect. The latter has been observed only with the impure commercially prepared acid. The impurity responsible has not yet been identified.

Work at present in progress indicates that the effects are wholly due to the presence of definite stable products formed in the course of the photoreaction ; with citric acid, pentabromoacetone ; with tartaric acid, an oxidation product, possibly aldehyde-tartronic acid or an isomer of this acid (*vide* Ciusa and Piergallani, *Atti. R. Acad. Lincei*, 1914, **7**, 23, 1, 811).

An after-effect has also been observed with sodium citrate and iodine (Dhar, *loc. cit.*).

We find, however, that under the conditions stated by Dhar (*J. Phys. Chem.*, 1928, **32**, 1308; 1929, **33**, 850) no measurable reaction takes place in visible light when the reactants are carefully purified, but that there is strong photocatalysis in the presence of traces of manganese and less so in the presence of iron. This reaction shows an after-effect. In the course of the photoreaction a solid substance is precipitated which appears to be identical with the hexaiodo-acetone prepared by Lederer (*Fortschritte der Theerfarbenfabrikation*, **6**, 709).

One of us (T. N. S.) is highly thankful to the Lucknow University for the award of a research fellowship which enabled him to undertake the work.

CHEMICAL LABORATORY,
LUCKNOW UNIVERSITY,
LUCKNOW.

*Received May 7, 1943.*

# RAMAN SPECTRA OF SOME COMPLEX HALIDES OF MERCURY

By M. R. Nayar and J. R. Saraf

Raman spectral evidence has been obtained for the existence of $HgCl_3'$ ion in addition to that for the molecule or ion like $HgCl_2$ and $HgCl_4''$.

Compounds of the type $K_2HgCl_4$ giving rise to the ion $HgCl_4''$ are well known. If, however, one molecule of $HgCl_2$ is mixed with one molecule of KCl we expect to get either (*i*) a mixture of $K_2HgCl_4$ and $HgCl_2$, or (*ii*) compound of the type $KHgCl_3$ giving rise to the ion $HgCl_3'$. The present work aims at deciding between these two alternatives.

It may, however, be mentioned that the previous workers (Krishnamurti, *Indian J. Phys.*, 1931, **6**, 7; Braune and Engelbrecht, *Z. physikal. Chem.*, 1930, **11B**, 409; Bernstein and Martin, *Trans. Roy. Soc. Canada*, 1937, **31**, III, 95) favoured the alternative.

The investigation has been extended to the study of the compound of the type 2KBr. $HgCl_2$ and to the complex compounds formed by $HgBr_2$ and $HgI_2$ on the addition corresponding alkali halide.

## RESULTS

The following table gives Raman frequencies in $cm^{-1}$ and their relative intensities. The exciting radiation is λ 4358·34 of the mercury spectrum. The shifts marked with a single asterisk denote that these have been confirmed by the line obtained by excitation with λ 4046·5 or λ 5461·73, while those marked with double asterisks show that the frequencies have been measured microphotometrically. Aqueous solutions have been used. of the The following notations are also used.

(v. s. = very strong ; s = strong ; m = medium ; w = weak)

| Substance. | | Authors' data. | Braune & Engelbrecht. | Bernstein & Martin. |
|---|---|---|---|---|
| $HgCl_2$ | (crystal) | *320·5 (v. s.) | | |
| | (soln.) | **330·5 (m) | 315-327 | |
| ½KCl.$HgCl_2$ (soln.) | | 318 (s) | | |
| KCl.$HgCl_2$ ,, | | **300 (m)<br>328 (w) | | |
| HCl.$HgCl_2$ ,, | | 304 (m)<br>331 (w) | | 265<br>302 |
| 1½KCl.$HgCl_2$ ,, | | 273 (m)<br>300 (m) | | |
| 2KCl.$HgCl_2$ | (crystal) | 273 (m) | | |
| | (soln.) | *,**274·4 (s) | 266 | |
| 2HCl.$HgCl_2$ (soln.) | | 273·7 (s) | | 265 |
| 2KBr.$HgCl_2$ (soln ) | | *178 (v. s.) | | |
| $HgBr_2$ (crystal) | | *193 (v. s.) | 187 | |
| 2KBr.$HgBr_2$ (soln.) | | *172 (s) | 166 | |
| 2KI.$HgI_2$ ,, | | 126 (s) | 126 | |

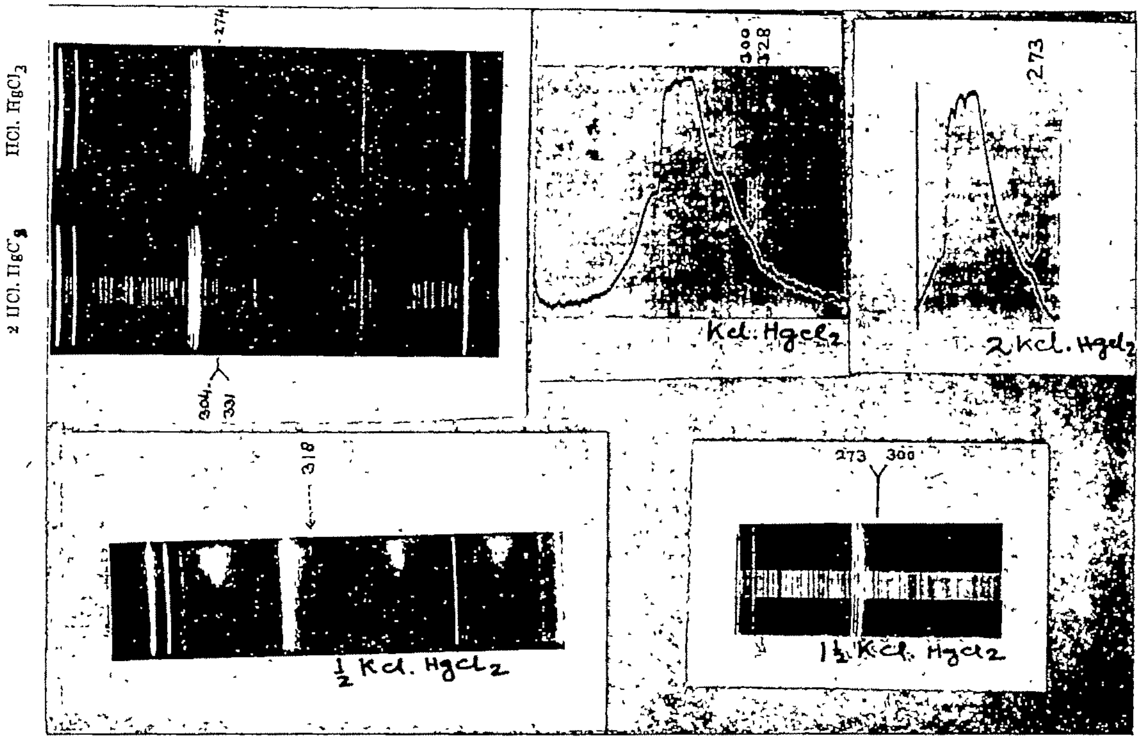
## DISCUSSION

*Mercuric Chloride and its Complex Compounds.*—The frequency due to $HgCl_2$ molecule is evidently $\Delta\nu$ 330. On the addition of one molecule of KCl or HCl there appears a new line at $\Delta\nu$ 300 together with that for $HgCl_2$ *viz.*, $\Delta\nu$ 330 which is very weak. The new line $\Delta\nu$300, therefore, seems to be characteristic of $HgCl_3'$ ion.

On further addition of one molecule of KCl or HCl to KCl. $HgCl_2$ or HCl.$HgCl_2$, the reduced frequency observed above is further reduced to $\Delta\nu$ 274, while all the other lines disappear. The line $\Delta\nu$ 274 should, therefore, be attributed to $HgCl_4''$ ion. We thus have the following characteristic frequencies.—

| | |
|---|---|
| $HgCl_2$ | $\Delta\nu$ 330 cm.$^{-1}$ |
| $HgCl_3'$ | 300 ,, |
| $HgCl_4''$ | 274 ,, |

Although Braune and Engelbrecht worked with five different solutions of composition 0·43KCl.$HgCl_2$, 0·86KCl.$HgCl_2$, 1·29KCl.$HgCl_2$, 2·36KCl.$HgCl_2$ and 8·6KCl.$HgCl_2$, the measurement of only one plate has been recorded presumably that corresponding to the last solution containing an over-excess of KCl (8·6 mols. of KCl) and hence giving rise to the most intense Raman line. They apparantly took it for granted that the frequency shift of the new line was the same in every plate. If measurements had been made on all the plates they would have arrived at a different conclusion.



Our obsetvations are in qualitative, and in some respects quantitative agreement with those of Bernstein and Martin who noted that "there is a gradual decrease in the frequency shift of $HgCl_2$ as the amount of HCl is increased" (Hibben, "Raman Effect and its Chemical Applications," 1939, p. 459). These authors give 265 for the frequency of $2HCl. HgCl_2$ and $\Delta\nu$ 302 for $HCl. HgCl_2$. The value 302 agrees excellently with the mean of our results for $KCl.HgCl_2$ (300) and $HCl.HgCl_2$ (304). The discrepancy between the results for $2KCl. HgCl_2$, *viz.* 265 (their value) and 274 (our value) is to be attributed to the composition of the solutions used. While we employed integral molecular proportions, they employed non-integral ratios of HCl and $HgCl_2$. However the difference is only nine units.

Thus while we agree with Braune and Engelbrecht that a solution of $HgCl_2$ containing a large excess of KCl (or HCl) gives a single line due to $HgCl_4''$ ion, we entirely disagree with them on the point that the new line given by, say 0·86KCl $HgCl_2$ is the same as that given by 2·36$KCl.HgCl_2$ or 8·6$KCl.HgCl_2$.

The evidence for the existence of $HgCl_3'$ ion is further furnished by the results obtained from intermediate mixtures such as $\frac{1}{2}KCl. HgCl_2$ and $1\frac{1}{2}KCl. HgCl_2$.

$\frac{1}{2}KCl{\cdot}HgCl_2$.—This might be regarded as either an equimolecular mixture of $HgCl_2$ and $KHgCl_3$ or a complex compound of the formula $KHg_2Cl_5$ or a mixture of $K_2HgCl_4$ and $HgCl_2$ in the ratio of 1 : 3.

The last possibility is ruled out because there is no line corresponding to $HgCl_4''$ ions. The observed shift is $\Delta\nu$ 318 with a width of 24 $cm^{-1}$. The observed frequency is significantly near the mean of the frequencies 330 and 300, that is of those attributed to $HgCl_2$ molecule and $HgCl_3'$ ion respectively. The question whether the line is a doublet can only be decided by a microphotograph which it was not possible to take in this particular case.

There is also the second alternative *viz.*, the complex $Hg_2Cl_5'$ ion. This perhaps should give a more complicated spectrum.

The evidence obtained from $1\frac{1}{2}KCl. HgCl_2$ is more convincing.

$1\frac{1}{2}KCl. HgCl_2$.—If this was regarded as an equimolecular mixture of $KHgCl_3$ and $K_2HgCl_4$ it should give rise to two lines of $\Delta\nu$ 300 and 274 of equal intensity. This was exactly what was observed. The two lines could be distinguished under the microscope and hence no microphotograph was necessary. Microphotometric records were obtained only for $HgCl_2$, $KCl. HgCl_2$ and $2KCl. HgCl_2$.

*Chemical Evidence.*—Chemical evidence for the existence of compounds like $KHgCl_3$ and $HHgCl_3$ is not lacking. Crystals of composition $HHgCl_3$ were prepared by Davy while the anhydrous salt $KHgCl_3$ was obtained by Linebarger (Mellor, "Treatise on Inorganic Chemistry", 1923, IV, 848, 856). The existence of compounds like $H_2HgCl_4$ and $K_2HgCl_4$ is well known.

$2KBr. HgCl_2$.—The shift obtained is $\Delta\nu$ 178, those given by $K_2HgBr_4$ and $K_2HgCl_4$ being 172 and 274 respectively. The proximity of the observed shift to that obtained with $K_2HgBr_4$ excludes the possibility of considering the substance as a mixture of $K_2HgBr_4$ and $K_2HgCl_4$. The formation of the compound $K_2Hg(ClBr)_2$ is also similarly to be excluded.

$2KBr. HgBr_2$ *and* $2KI. HgI_2$.—$2KBr. HgBr_2$ and $2KI. HgI_2$ give shifts at $\Delta\nu$ 172 and 126 respectively and represent the vibration frequencies of the ions $(HgBr_4)''$ and $(HgI_4)''$. Solutions of the type $KBr. HgBr_2$ and $KI. HgI_2$ in sufficient concentration could not be prepared and it was not possible to obtain evidence for the formation of the ions of the type $HgBr_3'$ and $HgI_3'$.

LUCKNOW UNIVERSITY.

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# ISOLATION OF PURE POTASSIUM NITRITE FROM THE COMMERCIAL SUBSTANCE

By Trambaklal Mohanlal Oza and Bhaskar Ramakrishna Walavalkar

Fairly appreciable quantities of pure potassium nitrite have been isolated from the Merck's pure potassium nitrite containing about 92% of the substance. When a concentrated aqueous solution of the substance is cooled in a freezing mixture of ice and ammonium chloride pure nitrite or mixtures of nitrite and nitrate richer in nitrite than the original substance crystallises out so that pure nitrite becomes separated on fractional crystallisation.

The melting point of the substance and its degrees of dissociation are ascertained and the solubility of the substance at the melting point of ice and the cryohydric point of ice and ammonium chloride are determined.

Numerous attempts have been made to prepare potassium nitrite in a pure state (Gay Lussac, *Ann. chim. phys.*, 1816, **27**, *i*, 394 ; Lang, *J. prakt. Chem.*, 1862, **86**, 296 ; Schwarz, *Dingler's J*, 1869, **191**, 397 ; Persoz, *Chem. Zentrl.*, 1878, 157 ; Muller and Pauly, *Arch. Pharm.*, 1879, **14**, 245 ; Warren, *Chem. News*, 1892, **66**, 190, 204 ; Divers, *J. Chem. Soc.*, 1899, **1**, 85 ; Milbauer and Jaderic, *Chem. Obzor.*, 1926, **1**, 16, 22 ; Slavina, *Trans. Inst. Pure Chem Reagents Moscow*, 1930, **10**, 21).

One of us made attempts to prepare pure potassium nitrite required for the study of its thermal decomposition (Oza and Shah, *J. Univ. Bom.*, 1942, **11**, *iii*, 70) by the double decomposition method with silver nitrite but the method was found to be both tedious and incapable of yielding appreciable amounts because of the low solubility of silver nitrite in water. Moreover, it was found in agreement with Divers (*loc. cit.*) that the nitrite thus prepared was greyish presumably due to contamination with silver chloride. He, therefore, tried the fractional crystallisation method with the commercial nitrite and was successful in separating pure potassium nitrite therefrom. We have now collected the results for presentation. The method, it will be seen from the results, is capable of giving commercial yields.

## EXPERIMENTAL

*Material.*—Merck's pure potassium nitrite worked upon was found to contain on analysis 92·7% potassium nitrite, the rest being potassium nitrate and chloride (trace).

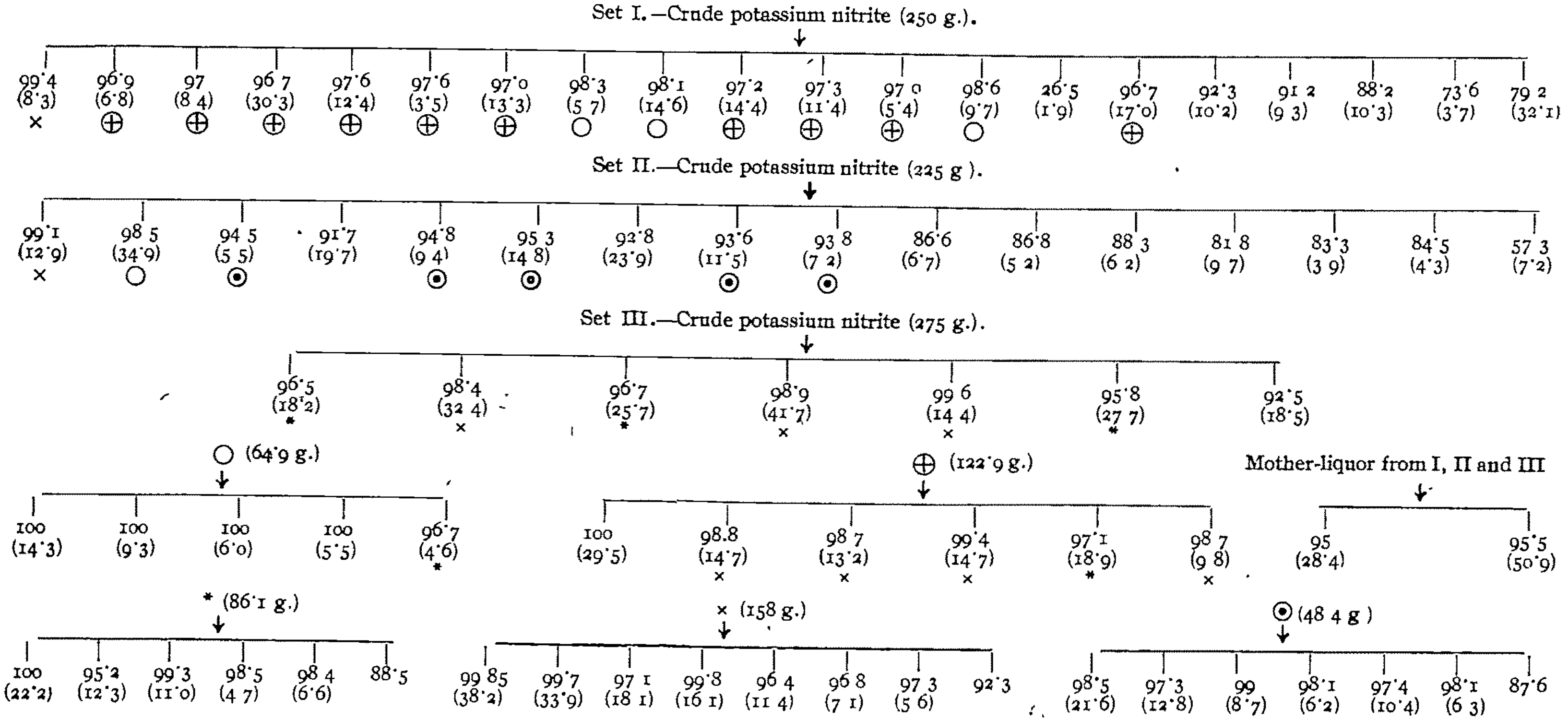
*Procedure and Analysis.*—A beaker containing a concentrated solution of the commercial substance (sp. gr. 1·615) was cooled in a finely ground intimate mixture of ice and ammonium chloride, the liquors being stirred during the process of cooling. When a sufficient crop of crystals separated, the contents of the beaker were rapidly filtered under the vacuum of the hyvac pump. The mother-liquors adhering to the solid were squeezed out by pressure. The solid was taken out and spread in a dish and kept in a desiccator over sulphuric acid to dry. The mother-liquors were concentrated in an oven maintained at 50-60° and when appropriate concentration was attained they were subjected to the freezing action. Several lots of crystals were separated in this way, and then purity tested with $KMnO_4$.

The results of experiments on three different sets are given in Table I. Brackets contain approximate mass of the particular lot whose analytical result ($KNO_2$ content %) is stated. The results are in serial order from left to right.

## TABLE I

*Fractional crystallisation of potassium nitrite*

Lots marked similarly are mixed together for subsequent crystallisations and results of these given under the sign



## TABLE II

*Degrees of dissociation of potassium nitrite*

| Dilution $v$ (litres) | Depression observed | $\alpha$ | $\alpha'$ |
|---|---|---|---|
| 4 | 0·845 | 0·798 | — |
| 8 | 0·43 | 0·836 | — |
| 16 | 0·22 | 0·88 | 0·86 |
| 36 | 0·10 | 0·93 | 0·91 |
| 72 | 0·052 | 0·99 | — |

## TABLE III

*Solubility of potassium nitrite*

| Temp. | Potassium nitrite |  | Potassium nitrate |  |
|---|---|---|---|---|
|  | I | II | I | II |
| M. p. of ice | 3·45 g. mol/100 | 3·43 g. mol/100 (3·29 at 0°) | 0·1317 g. mol/100 | 0·1317 g. mol/100 (0·130 at 0°) |
| Cryohydric point of ice and $NH_4Cl$ | 3·15 g. mol/100 | 3·18 g. mol/100 (3·16 at −10°) | — | — |

Working with one and a half pound of potassium nitrite 85 g. of chemically pure nitrite have thus been isolated by us. The analysis of the pure substance is given as :—

0·1130 G. substance gave 0·1144 g. of $K_2SO_4$ ; giving K=0·0512 g.
,, $KNO_2$ requires K=0·0518 g. K (calc.) =45·8 ; K (found)=45·3%.
0·0668 G. substance required 15·7 c.c. of 0·1 N-$KMnO_4$, giving $NO_2$=0·0361 g.
,, $KNO_2$ requires $NO_2$=0·0361 g. $NO_2$ (calc.) =54·1 ; $NO_2$ (found)=54·1%.

*The Melting Point of Pure Potassium Nitrite.*—Conflicting figures are found in literature for the melting point of pure potassium nitrite ; Ostwalds (*Internat. Congress Appl Chem.*, 1912, **8**, *ii*, 175) gives m.p. 297·5 ; Von Leugyal (*Naturwiss.*, 1933, **21**, 848) gives 419° ± 3 for 96-97% potassium nitrite.

Melting point was determined by taking the powdered substance in a test tube and heating it in an electric furnace. The test tube was placed inside a wider test tube which served as an air jacket and the temperature of melting determined by the help of mercury in a silica thermometer (650°). The liquid state was found to make its appearance first at 410° but the cooling curve of the liquid gave a more accurate m.p. of 407-408°.

*Properties of Potassium Nitrite.*—The substance separates in small thick prismatic crystals forming a coherent pale yellow sticky mass if not loosened before drying. When ground in a mortar it becomes powdery It is hygrocospic and does not contain any water of crystallisation.

*Degrees of Dissociation of Potassium Nitrite.*—Ray and Mukherjee (*Proc. Chem. Soc.*, 1910, **26**, 173) determined the degrees of dissociation of pure potassium nitrite by the conductivity method at two different dilutions. We have determined the same by the freezing point method, at dilutions equal to and other than those used by Ray. The results are given in Table II. The last column ($\alpha'$) contains Ray's results and it will be seen that the results agree within the range of expected agreement.

*The solubility of potassinm nitrite* at the melting point of ice and at the cryohydric point of ice and ammonium chloride has been determined. Standard method (Reilly and Rae, "Physico-chemical Methods ", p. 415) was used and the amount of potassium nitrite in the liquid phase was determined both by the evaporation and the chemical methods.

Temperature constancy was ensured in the following way. A large vacuum flask, wider in the body than at the mouth, was taken and its bark cork was drilled with five holes, two to contain saturated solutions of potassium nitrite, one to contain a saturated solution of potassium nitrate, a middle one to contain Beckmann thermometer and an outer one to contain a large stirrer. The thermometer indicated a constant temperature for hours together. Potassium nitrate solution froze completely at the cryohydric temperature so that its solubility at this temperature could not be determined. The results obtained are given in Table III. The figures in brackets are from the International Critical Tables at 0° and at -10°.

The results show that a redetermination of the solubility of pure potassium nitrite is necessary. The results in the International tables are due to Ostwald so that presumably his results were obtained with the nitrite of melting point 297·5° (*loc. cit.*).

The system $KNO_3-KNO_2-H_2O$ is being studied from the standpoint of the phase rule with a view to ascertaining the exact conditions of temperature and concentration suitable for the isolation of pure potassium nitrite.

We have pleasure in expressing our thanks to Prof. R. L. Alimchandani for his interest in the work and for facilities.

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*Received March 23, 1943.*

# A NOTE ON MERCURY DIALLYL

By K. V. Vijayaraghavan

The isolation of mercury diallyl by the action of sodium stannite on allyl mercuric iodide has been described by the author (*J. Indian Chem. Soc.*, 1940, **17**, 589). It has been found that mercury diallyl is also formed by the action of other reagents on allyl mercuric iodide.

On treating allyl mercuric iodide with an excess of a concentrated solution of potassium cyanide the characteristic smell of mercury diallyl was immediately noticed. Gradually all the allyl mercuric iodide disappeared and a colourless heavy liquid settled at the bottom and the aqueous layer was quite clear. The mercury diallyl was extracted with ether. The product was confirmed to be mercury diallyl by adding an ethereal solution of bromine when allyl mercuric bromide was obtained, m.p. 124-25° (decomp.).

$$2C_3H_5HgI + 4KCN \longrightarrow Hg(C_3H_5)_2 + K_2Hg(CN)_4 + 2KI.$$

It is surprising to note how Oppenheim (*Ber.*, 1871, **4**, 671) failed to observe this reaction. He reports that by the action of an excess of cold potassium cyanide solution on allyl mercuric iodide mercury, diallyl and a small quantity of a liquid, which explodes on heating, are formed. The smell of the substance is strong enough as not to escape one's notice and it does not explode but merely splits up into mercury and diallyl on heating.

Faint smell of mercury diallyl was noticed on keeping or gently warming aqueous suspensions of freshly prepared allyl mercuric iodide separately with sodium thiosulphate, sodium sulphide and potassium iodide. The action of all these reagents is very slight in the cold. On heating they all decompose allyl mercuric iodide, giving droplets of mercury, and mercury in aqueous solution as the corresponding complex salt. Probably the organic radical is split off.

Alcoholic solutions of allyl mercuric iodide were added to sodium thiosulphate and sodium sulphide separately. The ethereal extracts of these solutions contained no mercury diallyl. No intermediate organo-mercuric compound was present, for on adding sodium stannite, no mercury diallyl was formed. Only mercury was precipitated. The mercury seemed to have been in solution as purely inorganic complex salts, the organic part of the original molecule probably having undergone decomposition. An alcoholic solution of potassium iodide had no action on an alcoholic solution of allyl mercuric iodide in the cold but the smell of mercury diallyl was noticed on gently warming. On heating, the substance underwent decomposition forming potassium mercuri-iodide in solution An acetone solution of sodium iodide also gave a faint smell of mercury diallyl with allyl mercuric iodide in acetone but a greater part of the substance was present unchanged.

The author's thanks are due to Mr. Viswanathan for his kind interest in the work.

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Tambaram.

*Received May 19, 1943.*

# REVIEWS

**Polarography.**—By Prof. I. M. Kolthoff, Professor and Head of Division of Analytical Chemistry, University of Minnesota, Minneapolis, Minn, and J. J. Lingane, Instructor in Chemistry, University of California Berkeley, Cal. Published by Interscience Publishers, Inc., New York, N. Y. 1941, pages XVI + 510 with 141 illustrations. Price $ 6.

The book is intended "to present a complete and critical account of the present status of polarographic analysis...... ...and the newly developed 'amperometric titration' methods". The book is divided into eight parts and thirty-three chapters. The captions of these eight parts indicate the subject matter of the book and are: Introduction ; Theoretical Principles ; Apparatus and General Technique ; Inorganic Polarographic Analysis ; Organic Polarographic Analysis ; Biological Applications of Polarography, Voltammetry with Platinum Microelectrodes ; Amperometric Titrations.

The theoretical principles underlying these methods of analysis have been treated in some detail and the experimental evidence on which they are based have been amply cited. The recent work of the senior author and his collaborators has been drawn upon extensively. The book gives a full account of the present position of our knowledge regarding polarographic analysis. It will be found very useful by those interested in this branch of electrochemical analysis and more particularly by research workers in this subject. Its very wealth of detail, however, may cause embarrassment to those who are concerned more in the use of the method than in the details of numerous investigations some of which have not passed beyond the formative stage of development. It would be of great advantage if the subjects were presented in the next edition in two parts, one giving a brief outline of the theoretical principles, just sufficient experimental details for accurate results and only those examples of analyses where these methods have been found to be reliable and most useful. Detailed theoretical treatment and the various applications, where the method does not yield results which are quite unequivocal, might be dealt with in the other part. The theoretical background of the whole subject, though it has been considerably cleared up by recent work, seems to admit of considerable improvement in many places. One such topic is the interpretation of maxima. The fundamental relations in section 6 of the second chapter would, it is hoped, in due course be capable of a more direct theoretical treatment. One would have liked a more comprehensive discussion of the investigations on the electrocapillary curve which, as the authors have indicated, is of utmost significance in polarographic work.

Taking all in all, however, the book is a welcome publication and illustrates the great progress made in the development of these methods and their utility in which the authors and their collaborators have actively participated. In addition to the subject and author indices there is an appendix containing half-wave potentials of inorganic substances which will be found to be very useful.

The reviewer regrets the delay in reviewing the book partly due to pressure of work and partly for other reasons.

J. N. M.

**The Application of Absorption Spectra to the study of Vitamins, Hormones, and Co-enzymes**—By R. A. Morton, D.Sc,, Ph.D., F.I.C. Published by Adam Hilger, Ltd. 1942. pp. 226, Demy 8vo. Price. 28 Sh.

Biological and physical sciences are at present so intimately connected that much of the research and advanced teaching in biochemistry depends upon the competent use of physical methods and principles. Within the last twenty years, spectroscopy, as an implement of investigation, has developed into a unique position, almost indispensable for many fields of physical science. So the repercussion of its method and principle in other branches of studies is but natural. It was with Hartley's work in 1902 on the connection between absorption and the constitution of organic substances that the importance of absorption spectra in chemistry was fully established. Later, its application in biochemistry truly began, when Heilbron in 1927 started his investigation of cholesterol absorption. Since then biochemistry has been making extensive uses of this unique and versatile tool for its various problems of vitamins, enzymes, hormones, etc, involving

(a) Empirical identification of compounds available in quantities too minute to be examined by usual analytical method,

(b) Quantitative estimation of compounds with well defined characteristic absorption,

(c) Establishment of chemical structure, and

(d) Study of biochemical reactions.

Spectrophotometry consists of measuring the intensities of absorption exerted at different wave-lengths, by molecules in the path of the light. The mechanism of absorption varies with the wave-length of the radiation, or in other words, with the magnitude of the energy quantum. When a quantum of light is absorbed it may (*a*) effect dissociation, (*b*) raise an electron to a higher energy state, (*c*) bring about a change in inter-atomic vibrations or (*d*) cause a change in molecular rotation. Absorption spectra give most significant clues and wealth of informations about these.

The book under review is an enlarged and re-written edition of the earlier work by the author who is also widely known for his studies of vitamin, especially 'A'. The present volume covers a wider field and brings much of the knowledge of absorption spectra up-to-date. According to author the book is a 'contribution to the work of liaison' between professional and amateur spectroscopists. It also reviews many brilliant papers, distinguished by patient work, great skill and insight but it is more a record of small advances, the cumulative effect of which is prodigous in its implications. As the name suggests the book is mainly concerned with absorption spectra of vitamins, hormones, co-enzymes etc., in solution. It also makes borderland excursions into the studies of proteins and nucleoproteins, because all are closely interrelated to each other. Compounds of sterol groups have been subjected to most intensive spectroscopic studies because they include vitamin-D, the male and female sex hormones, bile acids, toad poisons and variety of carcinogenic compounds. In isolation of these substances and determination of their purity, chemical nature and structure absorption spectra played the most important role. It was almost a guide at every step of the process and gave the workers sufficient confidence that they are on the right track. Their studies have revealed many fundamental facts. Compounds differing strikingly in function are often structurally akin. Certain common skeleton such as *cyclo*pentenoperhydrophenanthrene has been found out which is common to sterols, bile acids, vitamin-D and the male and female sex hormones. It has also been established that selective absorption in the ultraviolet and visible is associated with unsaturated groupings like

$$-C=C-, \quad >C=O, \quad -N=N- \quad C_6H_5 \text{ etc.}$$

Concept of chromophoric groups has been introduced as a method for interpretation of these findings. The discovery and investigation of the properties of each of the vitamins have been accompanied by the measurement of its ultraviolet absorption spectra and the attempt to set up a quantitative correlation between the intensity of the absorption maxima and the biological potency of the vitamins. The correlation has been very successful in respect of vitamin-A but not so with other vitamins. Absorption spectra played a very important part in elucidation of vitamin-D problem and also of the structure and components of $B_1$. For the determination of chemical constitution of all other vitamins, use of absorption spectra has also been resorted to. Absorption spectrophotometry has greatly helped in establishing structure of respiratory enzymes and in following their activities in the living cells. The respiratory enzyme complex cytochrome which, through its ability to be reversibly oxidised and reduced, acts as a hydrogen carrier in the oxidative processes taking place in the living cell, has a characteristic absorption spectrum in the reduced form. The co enzymes DPN and TPN have been identified and quantitative estimation made with absorption spectra. With the older and usual enzyme technique, only the total effect of all cellular processes involved could be studied, but with spectrophotometry, each individual step can be isolated. This opens a new possibility in the enzyme chemistry.

The book will be highly useful to the biochemists, who having other main interests, find it necessary to make use of absorption spectra for the investigation of their own problems. A good knowledge of experimentation and interpretation of absorption spectra will be all the more imperative to the biochemists because with the advent of quantum mechanics, a great clarification of the theory of larger molecules in which biochemists are interested, has already began to take shape. The study of absorption spectra is, therefore, destined to be almost indispensable for biochemical investigations in future.

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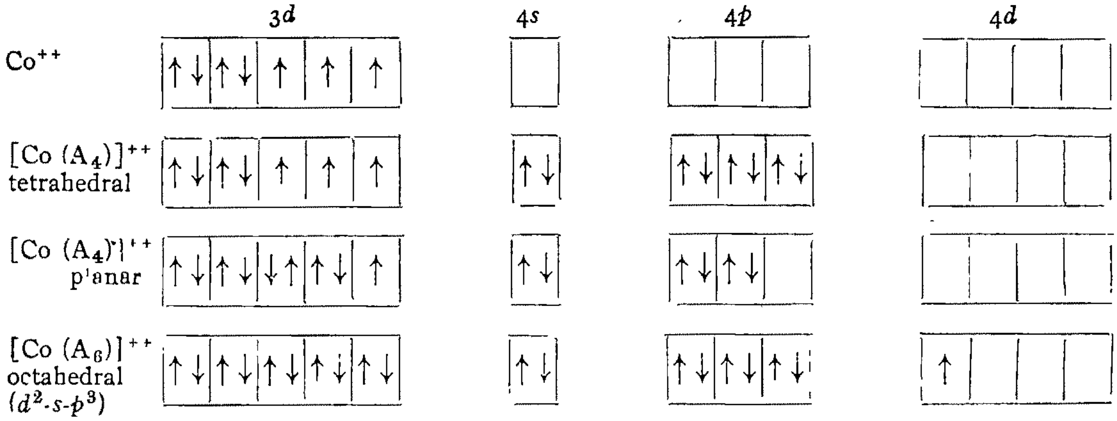
# MAGNETIC SUSCEPTIBILITY OF COBALTOUS COMPLEXES AND THEIR CONSTITUTION

By Priyadaranjan Rây and Sailaja Prasad Ghosh

Certain fairly stable cobaltous complexes of the penetration type have been prepared and their magnetic susceptibilities determined. The compounds studied are diaquo-cobaltous ethylenediamine*bis*acetylacetone, cobaltous ethylenebiguanidinium sulphate, cobaltous biguanidinium sulphate and its hydroxide. Of these, the preparation of the first compound was previously described by Morgan and Smith. The moment value of about 2·6 Bohr, found for these complexes, which is considerably lower than that of simple cobaltous ion (5·04 Bohr), furnishes definite evidence that they are of the penetration class with planar structure for the fourfold co-ordination and that the magnetic moment of cobaltous cobalt in these complexes differs from the theoretically expected value on the basis of $d$-$s$-$p^2$ hybrid bonds. The discrepancy is attributed to the incomplete quenching of the orbital moment of the unpaired electron in the complex.

The co-ordination complexes can in general be sharply divided into two classes from their magnetic behaviour, as was pointed out by one of us as early as 1928 (Rây, *J. Indian Chem. Soc*, 1928, **5**, 73; *Z. anorg. u. allg. Chem.*, 1928, **174**, 189). These were distinguished as Penetration (Einlagerung) and Associated (Anlagerung) complexes. In the former some of the shared electrons forming the co-ordinated bonds were supposed to enter the inner incomplete level of the central atom, while in the latter they were regarded to fill only the valency or the outermost levels. It was also suggested that in some of the associated complexes the co-ordinated addenda were held simply by electrostatic attraction. In later years Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225), on the basis of quantum mechanics, developed a comprehensive theory of complex compounds, which satisfactorily accounts for their magnetic behaviour and molecular configuration. According to Pauling, in sixfold complexes where $d^2$-$s$-$p^3$ hybrid bonds are formed with $d$-orbitals of a lower quantum number, the molecule assumes an octahedral structure with considerable reduction of the magnetic moment of the central paramagnetic ion, except, of course, in the case of chromium where it remains unchanged. In many cases, *e.g.*, for $Co^{3+}$, $Fe^{2+}$, $Pt^{4+}$, $Ir^{3+}$, $Rh^{3+}$, etc., the moment is reduced almost to zero and the molecule becomes diamagnetic. Where the bonds are of $s$-$p^3$-$d^2$ type with $d$-orbitals in the same quantum number as $s$ and $p$ orbitals, the configuration of the molecule remains octahedral, but there occurs practically no change in the magnetic moment of the central paramagnetic ion. Under these circumstances the complex ion may assume a resonating structure, with the co-ordination bonds resonating with ionic or ion-dipole bonds. For fourfold complexes with a bivalent central ion, Pauling assumes the possibility of two different space configurations, planar square or tetrahedral, with $d$-$s$-$p^2$ or $s$-$p^3$ bonds respectively. In the former a $d$-orbital of the penultimate level takes part in the bond formation. The tetrahedral configuration with all the bond orbitals in the same level ($s$-$p^3$) may, therefore, resonate with ionic or ion-dipole bond structure. Hence, the magnetic moment of the paramagnetic central ion remains practically unchanged in its tetrahedral complexes. In complexes with planar configuration, however, if as the result of bond formation there remains no unbalanced or unpaired electron in the molecule, the moment of the central paramagnetic ion practically vanishes and the molecule becomes diamagnetic. This is observed in the case of certain nickel complexes, characterised by red, yellow or orange colour, namely nickel dimethylglyoxime, potassium nickelocyanide, nickel biguanidines, etc.

In the case of cobalt, the bond formation for sixfold and fourfold complexes can, after Pauling, be illustrated as follows. The configuration of the simple cobaltous ion is also added for comparison.



[Arrows indicate the spin of the individual electrons in each orbital].

Almost all the cobalt complexes, that have already been examined magnetically, give practically the same moment for the central cobalt atom as that of the simple cobaltous ion. This suggests that the cobaltous complexes in general are of the associated type. Their physical and chemical properties also support this idea. As is well known, these associated cobaltous complexes are rather unstable and pass readily by oxidation into the cobaltic complexes, which are usually of the penetration type. But there are one or two cobaltous complexes, described in literature, whose colour (yellow or orange) and stability indicate that they are possibly of the penetration type, having planar configuration with $d$-$s$-$p^2$ bonds. Recenly, however, we have succeeded in preparing a few fairly stable cobaltous biguanide complexes of bright yellow colour, presumably of the penetration type (*J. Indian Chem. Soc.*, 1943, **20**, 291). It was, therefore, considered of great interest to determine their magnetic susceptibility with a view to ascertaining the configuration of their molecule For, it will be observed, from an examination of the electronic configuration given above, that planar cobaltous complexes with $d$-$s$-$p^2$ bonds, or an octahedral complex with $d^2$-$s$-$p^3$ bonds, having an unpaired electron in the molecule, should give a magnetic moment of 1·73 Bohr magnetons on the basis of Bose-Stoner's formula, $\mu_B = \sqrt{4S(S+1)}$, assuming that spin alone is effective. Whereas the moment of cobalt atom in its simple ion or associated complex, due to the presence of three unbalanced electrons, should, according to the above formula, give a moment of 3·87 Bohr magnetons. Actually, however, in the latter case the observed value is somewhat larger and is equal to 5·04 Bohr magnetons. This discrepancy is interpreted as a result of imperfect quenchig of orbital moment due to weak $l$-interactions. It follows, therefore, that the magnetic moment of the cabaltous ion will be profoundly altered (a reduction of $5{\cdot}04-1{\cdot}73=3{\cdot}31$ Bohr magnetons) by the formation of a penetration complex of planar square or octahedral type.

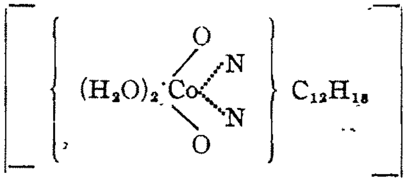
In what follows, the measurement of magnetic moment of these cobaltous complexes has been described and their results discussed.

## EXPERIMENTAL

Kahlbaum's nickel-free cobalt chloride was used in the preparation of all the following cobaltous complexes.

*Diaquo-cobaltous ethylenediamine*bis*acetylacetone* was prepared following the method described by Morgan and Smith (*J. Chem. Soc.*, 1925, 2034) ; $CoCl_2.6H_2O$ (1 mol , 48 g.) dissolved in 20 c.c. of hot water, and ethylenediamine*bis*acetylacetone (1 mol., 4·5 g.)and 8 c.c. of 5*N*-NaOH were mixed together. A green paste was formed. The mixture, on boiling, turned brownish yellow and a reddish orange crystalline product was obtained. This was filtered, washed with cold water and dried in air.

{Found: Co, 20·10, 20·55



requires Co, 18·58%}.

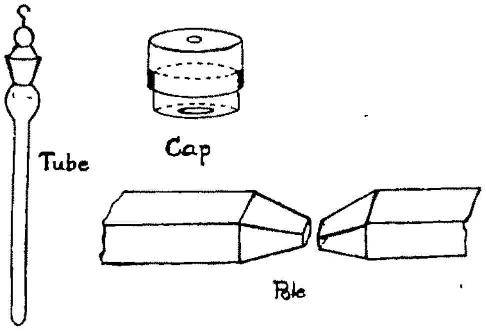
The result shows that the product is impure. Several samples were prepared with all possible care, but we could not get better results. The substance was always found to contain traces of brown products. It is insoluble in water, but dissolves readily in many organic solvents ; from the latter, however, it could not be recrystallised as the solution began to darken immediately.

*Cobaltous ethylenebiguanide sulphate* $[Co(C_6H_{16}N_{10})]\ SO_4.2\frac{1}{2}H_2O$, *cobaltous biguanide sulphate* $[Co(C_2H_7N_5)_2]SO_4.4H_2O$ and *cobaltous biguanide hydroxide* $[Co(C_2H_7N_5)_2](OH)_2$ were prepared as described in the previous paper (*loc. cit.*), and their purity verified by analysis.

### *Magnetic Measurements*

Susceptibility measurements were made according to Guoy's method. An electromagnet with its core made of Swedish soft iron and pole-pieces of the shape shown in the figure, fixed at a distance of 1·8 cm., was employed for these measurements. A current of about 6 amperes was found to be necessary for the magnetic saturation of the iron core, but as the field-strength with 5 amperes was only 6·5% lower, all measurements were made with the latter current to avoid undue heating of the coils. The current was taken from the main through an adjustable resistance and ammeter. A parallel circuit with a lamp was also arranged, which could momentarily be thrown in along with the main circuit just before the current was switched in or out of the magnet. This served to ensure a slow rise or fall of the current at the start or break of the main circuit, and thus to avoid high surge current which might damage the insulation of the coils by sparking. During the actual period of measurement, however, this branch circuit was kept always cut off from the main. The centre of the maximum field between the pole-pieces was determined by a topographical survey with a tube containing a column of a paramagnetic substance like copper sulphate. The tube containing the specimens for measurement was always suspended between the poles in such a way that its lower end coincided with this centre. The field-strength was found to be uniform within a stretch of 7 mm. below or above this

FIG. 1



[ Not to scale ]

point; the bottom of the specimen tube was, therefore, always in the region of maximum field even under oscillations during weighing. The field was found to be practically negligible at 8 cm. above this point. The specimen tubes were, therefore, always filled up to a height of at least 9 cm. A glass thread was used for their suspension from an adjustable hook at the bottom of one of the pans of a Bunge Analytical Balance A I, sensitive to 1/20th mg. The tube was provided with a glass stopper ending in a hook for suspension and tightly held in position by the ebonite cap as shown in the figure. The entire magnet was enclosed in a glass box with glass doors. The susceptibility was calculated from the following expression :

$$K = \frac{\chi_m \times m \times H^2_{\max}}{2l}$$

where $K$ = force exerted on the substance by the field in dynes, $\chi_m$ = mass susceptibility, $m$ = wt. of the substance in g., $H_{\max}$ = maximum field in gauss, $l$ = height in cm. of the substance column in the tube.

Hence, $$\chi_m = \frac{2l \times \text{change of weight in mg.}}{m \times H^2_{\max} \times 1{\cdot}019}.$$

Finally, correction should be made for susceptibility of the air displaced by the substance, as weighings were made in air. For this, a knowledge of the density of the substance examined is, however, necessary. But as this correction is very small in magnitude, it can be neglected in the case of paramagnetic substances. Whenever this correction became necessary the following expression was used :

$$\chi_m = \frac{2l \times \text{change of wt. in mg.}}{m \times H^2_{\max} \times 1{\cdot}019} + \chi^T_v / d_s,$$

where $d_s$ = density of the substance, T = the temperature of measurement (absolute) and $\chi^T_v$ = volume susceptibility of air at T. $H_{\max}$ was determined by using a number of standard substances like ferrous ammonium sulphate, chrome alum and copper sulphate, as accurate values for their mass susceptibilities are known. The use of nickel ammonium sulphate as standard, employed by some workers, was avoided, since values for its mass susceptibility, measured by different investigators, do not agree (*cf.* Jackson, *Phil. Trans.*, 1923, **A**, 224; Seres, *Ann. Physik*, 1933, **10**, 20, 441; Bartlett, *Phys. Rev.*, 1932, ii, **41**, 818). Since $\chi_m$ depends on the ratio $l/m$, substances in all cases were packed uniformly and tightly into the measurement tubes by gently ramming with a thin glass rod.

*Ferrous ammonium sulphate* (Scherring-Kahlbaum's *pro analysi* certified quality of the salt) was dissolved in cold water, acidified with a few drops of sulphuric acid and then precipitated by alcohol. The product was washed first with cold water, then with alcohol and finally dried in air. [Found : Fe (volumetrically), 14·23. Calc. Fe, 14·24 per cent]

*Chrome alum* was prepared from chemically pure potassium dichromate (Merck's *pro analysi* guaranteed reagent) and sulphuric acid (reagent-Kahlbaum) by reduction with alcohol. The product was then purified by recrystallisation from water by the addition of alcohol. The crystals were dried in air. [Found : Cr (volumetrically), 10·45. Calc. Cr, 10·42 per cent].

For *copper sulphate*, Scherring-Kahlbaum's sample of certified analytical reagent quality was used after careful recrystallisation. The crystals were dried in air. [Found : Cu (volumetrically), 25·49. Calc. Cu, 25·47 per cent].

$\chi_m$ for ferrous ammonium sulphate was calculated from Jackson's value (*Phil. Trans.*, 1924, **A**, 2241), $\chi_m\,(17\cdot3^\circ) = 32\cdot57 \times 10^{-6}$ and $\theta = -1^\circ$. The value for chrome alum was calculated from Haas and co-workers' value for $\mu_B = 3\cdot85$ with $\theta = 0^\circ$ and that of copper sulphate from $\mu_B = 1\cdot92$ with $\theta = -0\cdot7^\circ$ by the same authors (*J. Commun. physic. Lab. Univ. Leiden*, 208c, 210d).

The values of $H_{max}$ obtained are shown in the following table.

| Substance. | Temp. | $\chi_m$ | $H_{max}$ in gauss. |
|---|---|---|---|
| $FeSO_4.(NH_4)_2SO_4.6H_2O$ | 32° | $31\cdot1 \times 10^{-6}$ | $10\cdot15 \times 10^3$ |
| ,, ,, ,, ,, | 35 | $30\cdot8$ | $10\cdot08$ |
| $KCr(SO_4)_2.12H_2O$ | 31 | $12\cdot01$ | $10\cdot21$ |
| ,, ,, ,, | 33 | $12\cdot04$ | $10\cdot14$ |
| ,, ,, ,, | ,, | ,, | $10\cdot20$ |
| $CuSO_4.5H_2O$ | $32\cdot5$ | $5\cdot84$ | $10\cdot21$ |
| | | Mean | $10\cdot16 \times 10^3$ |

The mass susceptibility of the substances under investigation was calculated from the expression given above with the value of $H_{max} = 10\cdot16 \times 10^3$ gauss, and ignoring the air correction which is obviously negligible for paramagnetic bodies.

1. *Diaquo-cobaltous ethylenediaminebisacetylacetone* $[(H_2O)_2.Co.O_2N_2C_{12}H_{18}]$.

   $\chi_m = 7\cdot91 \times 10^{-6}$. Temp. $= 30^\circ$. $\chi_M = 317 \times 7\cdot91 \times 10^{-6} = 2509 \times 10^{-6}$. Correction for diamagnetism $= +\,156\cdot5 \times 10^{-6}$. $\chi_A = 2665\cdot5 \times 10^{-6}$. $\mu_B$(corr.) $= 2\cdot55$. A second sample gave $\chi_m = 6\cdot926 \times 10^{-6}$. Temp. $= 31^\circ$. $\chi_M = 2194 \times 10^{-6}$. Correction $= +156\cdot5 \times 10^{-6}$. $\chi_A = 2350\cdot5 \times 10^{-6}$. $\mu_B$(corr.) $= 2\cdot40$.

2. *Cobaltous ethylenebiguanidinium sulphate* $[Co(C_6H_{16}N_{10})]\ SO_4.2\cdot5H_2O$.

   $\chi_m = 6\cdot81 \times 10^{-6}$. Temp $= 26^\circ$. $\chi_M = 428 \times 6\cdot81 \times 10^{-6} = 2914 \times 10^{-6}$. Correction $= +190\cdot0 \times 10^{-6}$. $\chi_A = 3104 \times 10^{-6}$. $\mu_B$(corr.) $= 2\cdot74$.

3. *Cobaltous biguanidinium hydroxide* $[Co(C_2H_7N_5)_2](OH)_2$.

   $\chi_m = 8\cdot268 \times 10^{-6}$. Temp $= 30^\circ$. $\chi_M = 295 \times 8\cdot268 \times 10^{-6} = 2439 \times 10^{-6}$. Correction $= +110\cdot04 \times 10^{-6}$. $\chi_A = 2549\cdot8 \times 10^{-6}$. $\mu_B$(corr.) $= 2\cdot49$.

4. *Cobaltous biguanidinium sulphate* $[Co(C_2H_7N_5)_2]\ SO_4.4H_2O$.

   $\chi_m = 6\cdot787 \times 10^{-6}$. Temp. $= 30.2^\circ$. $\chi_M = 429 \times 6\cdot787 \times 10^{-6} = 2912 \times 10^{-6}$. Correction $= +185\cdot8 \times 10^{-6}$. $\chi_A = 3097\cdot8 \times 10^{-6}$. $\mu_B$(corr.) $= 2\cdot75$.

Corrections for the diamagnetism of other atoms, groups or ions in the complex cobaltous compounds together with any constitutive factors, as well as for the inherent diamagnetism of the cobaltous ion itself, were made in the molecular susceptibility in each case. The diamagnetic susceptibility for the cobaltous ion is assumed to be equal to that of zinc ion due to close agreement between their ionic radii. The values employed for $Co^{++}$ and $SO_4''$ ions are $-12\cdot8 \times 10^{-6}$ and $-39\cdot0 \times 10^{-6}$ respectively (Kido, *K. Sci. Rep. Tohoku Imp. Univ.*, 1932, **21**, 149). For other atoms or groups as also for any constitutive factor, corrected Pascal's values were adopted. From the corrected susceptibility of the central cobalt atom, its magnetic moment was calculated according to the equation :

$$\mu_B = 2\cdot84\,\sqrt{\chi_A \times T},$$

where $\chi_A$ = corrected atomic susceptibility for cobalt.

## DISCUSSION

Though the substance No. 1 could not be obtained in a pure state, still its magnetic moment approaches closely the values found for the more or less pure compounds, Nos 2, 3 and 4. These latter again do not give the same value, which may be due to the fact that they are not possibly magnetically pure. It may also result from a possible difference in $\theta$ corrections for the compounds. But these have not been determined. In any case it gives an idea about the order of the moment value for a central cobalt atom in a co-ordinated cobaltous complex of the penetration type. As an average we may take it to be equal to 2·66 Bohr magnetons, which, it is believed, will not differ appreciably from the actual value of the pure compounds.

We may now compare this with the theoretical moment-value for cobalt in a cobaltous complex with $d$-$s$-$p^2$ or $d^2$-$s$-$p^3$ bonds on the basis of Pauling's theory. According to the latter the moment of such a complex will be due to the presence of one unpaired electron as shown in the figure, already described (*vide supra*). On the basis of Bose-Stoner's formula, the moment should be given by :

$$\mu_B = \sqrt{4S(S+1)} = 1{\cdot}73.$$

On the other hand, if we assume that the orbital moments are not quenched, but free to orient independently as the spin moment, then the molecule should give, as required by the formula

$$\mu_B = \sqrt{4S(S+1) + L(L+1)},$$

a moment value of 3 Bohr magnetons, assuming that the lone electron occupies a 3-$d$ orbital in the planar and a 4-$d$ in the octahedral complex with $L$-value equal to 2. The experimental value of 2·66 Bohr magnetons seems to suggest that the $L$-moment is only partially quenched in these cobaltous complexes. It is of interest to recall in this connection that the moment of 5·04 Bohr for the cobalt atom in simple cobaltous ion, $Co^{++}$, or in its associated complexes, also does not follow Bose-Stoner's formula, but rather the one based on the free orientation of the $L$-moment, which requires 5·2 Bohr. In any case the profound alteration of the moment of $Co^{++}$ from 5·04 to 2·66 Bohr in the above-discussed complexes furnishes a strong evidence that they are of the penetration type, and are all fourfold complexes with planar structure having more or less the same moment. The bright yellow colour of these cobaltous complexes resembling those of the corresponding nickel compounds strongly supports this view. It may also be pointed out in this connection that in its triple nitrites, *e.g.*, $K_2Ca[Co(NO_2)_6]$, the central cobalt atom shows a magnetic moment of about 1·73 Bohr magnetons as required by Pauling's theory (*Rây and Sahu,* private communication, also Pauling "The Nature of the Chemical Bond", 1940, p. 116). This indicates that in these anionic octahedral complexes the orbital moment of the central cobalt atom is completely quenched as might be expected from their electronic configuration in which the unbalanced electron, responsible for magnetic moment, is raised to the outermost 4-$d$ level, where it is fully exposed to the influence of the field of the neighbouring atoms and ions (*vide* figure above). The configuration of the fourfold planar cobaltous complexes, on the other hand, shows that the unbalanced electron in their case lies much deeper in the 3-$d$ level and is thereby protected from the field of the surrounding atoms or ions, making the $L$-moment free to orient in the magnetic field. The effect might also be dependent upon the strength of the spin-orbit coupling, as well as upon that of the electric field of the neighbouring atoms or ions, which varies with their nature and their distance.

We take this opportunity to express our sincere thanks to Mr. Shyamadas Chatterjee, M.Sc., of Bose Institute for his ungrudging assistance in the construction of the electro-magnet.

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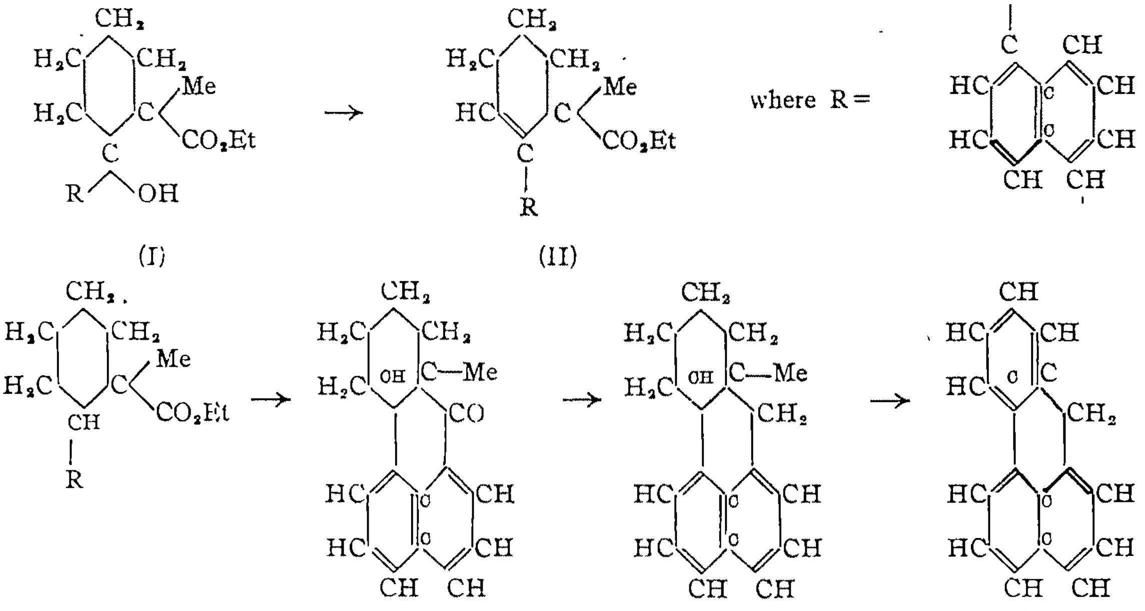
# A NEW ROUTE TO POLYCYCLIC COMPOUNDS HAVING ANGULAR METHYL GROUP. SYNTHESIS OF *ISO*CHRYSOFLUOREN

By Nripendra Nath Chatterjee and Hitendra Bhusan Roy

The synthesis of *iso*chrysofluoren is described.

Many important complex terpenes, the sterols and certain of the alkaloids are stated to have an alkyl group attached to a carbon atom which is itself a common member of two ring systems. Synthesis of such complex bodies will only be possible by a process which will ultimately lead to a compound having angular methyl group. Investigation described below was undertaken with a view to developing one such method.

α-Naphthyl magnesium bromide is allowed to react with ethyl 2-methyl*cyclo*hexanone-2-carboxylate to yield ethyl 1-α-naphthyl-2-methyl*cyclo*hexanol-2-carboxylate (I). This on dehydration yields ethyl 1-α-naphthyl-2-methyl*cyclo*hexene-2-carboxylate (II). This unsaturated ester is reduced catalytically (Roger-Adam's platinum oxide catalyst) to yield ethyl 1-α-naphthyl-2-methyl*cyclo*hexane-2-carboxylate (III). 1-α-Naphthyl-2-methyl*cyclo*hexane-2-carboxylic acid, obtained after hydrolysis of the ester (III), is converted into acid chloride by the action of thionyl chloride and subjected to the action of aluminium chloride to yield methylhexahydro*peri*-benzanthron (IV). This derivative is reduced by means of phosphorus and hydriodic acid when methylhexahydro*iso*chrysofluoren (V) is obtained. The compound (V), when heated with selenium, yields *iso*chrysofluoren (VI).



(I) (II)

(III) (IV) (V) (VI)

## EXPERIMENTAL

*Ethyl* cyclo*Hexanone-2-methyl-2-carboxylate.*—Methylation of ethyl *cyclo*hexanone 2-carboxylate by the method of Kotz and Michels (*Annalen*, 1905, **350**, 210) was found to be unsatisfactory as by this method, a substance free from ferric chloride colouration was never obtained. Chung, Tien Huong (*Ber.*, 1935, **68**, 164) using sodium methoxide in methyl alcoholic solution obtained the methylated compound in somewhat better yield. But by the following method a product was obtained which gave no colouration with ferric chloride and the yield was almost quantitative.

A mixture of sodium (5 g.), benzene (250 c.c.) and ethyl *cyclo*hexanone 2-carboxylate (34 g.) was left overnight. The sodium salt, which separated, was then refluxed with methyl iodide (18 c.c.) for 4 hours on the water-bath and worked up in the usual manner, b.p. 104-105°/6-7 mm.

*Ethyl* 1-α-*Naphthyl-2-methyl*cyclo*hexanol-2-carboxylate* (I).—When an ethereal solution of ethyl *cyclo*hexanone-2-methyl-2-carboxylate (15 g.) was treated with α-naphthyl magnesium bromide (from 12 c.c. of α-bromonaphthalene and 1·9. g of magnesium) a gelatinous precipitate separated. The mixture was left overnight and decomposed with cold dilute sulphuric acid, extracted with ether, the ethereal extract washed several times with water, and the product distilled at 220-25°/6 mm. as a viscous liquid. (Found: C, 76·4; H, 7·8. $C_{20}H_{24}O_3$ requires C, 76·9; H, 7·69 per cent).

*Ethyl* 1-α-*Naphthyl-2-methyl*cylco*hexene-2-carboxylate* (II).—A mixture of ethyl-1-α-naphthyl-2-methyl-2-carboxy*cyclo*hexanol (41 g.) and pyridine (22·8 c.c.) in ether (83 c.c.) was cooled in an ice-bath and thionyl chloride (10 c.c.) was added drop by drop with constant shaking. It was then left at ordinary temperature for 2 hours. The ethereal layer was separated after addition of ice-water, washed successively with cold dilute sulphuric acid, cold dilute caustic potash and water. After drying the ether was evaporated and the product was repeatedly distilled in vacuum and the portion coming at 210-20°/6 mm. was collected. (Found: C, 81·1; H, 7·4. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·4 per cent).

*Ethyl* 1-α-*Naphthyl 2-methyl*cyclo*hexane-2-carboxylate* (III).—Freshly distilled unsaturated ester (II) (11 g.) was shaken in an alcoholic solution with platinum oxide (3 g.) for about one month when the calculated quantity of hydrogen was absorbed. The product after working up in the usual manner was distilled, b. p. 208-10°/6 mm. (Found: C, 81·5; H, 8·2. $C_{20}H_{24}O_2$ requires C, 81·08; H, 8·1 per cent).

1-α-*Naphthyl-2-Methyl*cyclo*hexane-2-caiboxylic Acid.*—The above ester was refluxed with three times the calculated quantity of alcoholic potash (10%) in a water-bath for 2 hours. Alcohol was removed after dilution, acidified, and the acid extracted with ether. The acid was removed from the ether extract by treating with sodium bicarbonate solution. On acidification the free acid was liberated. It was extracted with ether, dried with sodium sulphate, and the solvent removed, b. p. 235-45°/7 mm. (Found: C, 80·2; H, 7·3. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·4 per cent).

*Methylhexahydro-peri-benzanthron* (IV).—The above acid (15 g.) was converted into its chloride by boiling for 3 hours with thionyl chloride (100 c.c.), excess of thionyl chloride being then removed on the water-bath under reduced pressure. An ice-cold carbon disulphide (100 c.c.) solution of the chloride was treated with anhydrous aluminium chloride (20 g.), kept at 0° for 3 hours, and then decomposed with ice and hydrochloric acid. After being washed with sodium carbonate solution it was dried, carbon disulphide removed and the residue distilled, b. p. 215-25°/4 mm. (Found: C, 87·0; H, 6·8. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2 per cent).

iso*Chrysofluoren* (VI).—The above ketone (2 g.), hydriodic acid (5 c.c., 50%) and red phosphorus (2 g.) were heated together for 8 to 10 hours under reflux. The product was extracted with ether, the ethereal solution washed with water and dilute alkali. On removing ether a gummy residue was left, which was heated with selenium for 30 hours at 300-40° and the product was converted into picrate, m.p. 110-11°. *iso*Chrysofluoren, regenerated from pure picrate, melted at 84° (lit. m.p. 84°, *cf.* Bally and Scholl, *Ber.*, 1911, **44**, 1656). (Found: C, 94·8; H, 5·2. Calc. for $C_{17}H_{12}$: C, 94·4; H, 5·5 per cent).

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# STUDIES ON ADSORPTION IN RELATION TO CONSTITUTION. PART II. ADSORPTION OF ORGANIC ACIDS ON ACTIVATED SILICA GEL

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Relationship between constitution and adsorption on active silica gel in the case of a large number of organic acids and the effect of substitution of polar groups on adsorption have been investigated.

Attempts have often been made to correlate the constitution of molecules with their adsorption on different surfaces. As early as 1896 Walker and Appleyard (*J. Chem. Soc.*, 1896, **69**, 1334) observed that the adsorption of acids on silk depended upon their chemical nature. Aromatic acids gave an adsorption of 23%, the adsorption of fatty acids was 6%, whilst the mineral acids occupied a mean position with an adsorption of 11−16%. Fromageot and Wurmser (*Compt. rend.*, 1924, **179**, 972) studied the adsorption of organic acids from aqueous solutions on charcoal and found that the amount of adsorption increased in an irregular manner with the number of carboxyl groups in the molecule. Schilow and Nekrassow (*Z. physikal. Chem.*, 1927, **130**, 65) found that the adsorption of fatty monobasic and saturated dibasic acids on active charcoal always increased with the number of carbon atoms in the molecule. They further found that the successive differences between members of the homologous series attained a maximum at the fifth or sixth member. Landt and Knop (*Z. physikal. Chem.*, 1932, **162**, 331) observed that aqueous solutions of monobasic acids displaced hydrochloric acid molecules adsorbed on charcoal in direct proportion to the number of carbon atoms contained in the molecule. Apart from the influence of the number of carbon atoms, the effect of introduction in the molecule of various active groups like $-OH$, $-SO_3H$, $-COOH$, $=CO$, $-CN$, $-Cl$, double bond etc., on adsorption has been investigated by various workers. Schilow and Nekrassow observed that the introduction of double bonds and other active groups always led to increased adsorption whilst the introduction of hydroxyl and sulphonic acid groups produced a diminished adsorption. The result with regard to hydroxyl group was corroborated by Linner and Gortner (*J. Phys. Chem.*, 1935, **39**, 35) but contrary to Schilow and Nekrassow, they found a decrease with double bonds.

The adsorption of aromatic acids has generally been found to be higher than that for aliphatic acids (Freundlich, "Colloid and Capillary Chemistry", 1926, p. 197). Thus, Ockrent (*J. Chem. Soc.*, 1932, 613) found that aqueous solutions of benzoic, salicylic, and toluic acids show a much stronger adsorption than corresponding solutions of monochloracetic, formic, and trichloracetic acids, on active charcoal. This is also borne out by the experiments of Schilow and Nekrassow who found the adsorption of monochloacetic acid to be 25%, whilst on the substitution of Cl by a phenyl group, the resulting phenylacetic acid gave an adsorption of 62·4%. Jain and Jha (*J. Indian Chem. Soc.*, 1940, **17**, 685) have found the adsorption of dibasic acids to increase with the higher members of the homologous series. They have, however, found a lower adsorption for phthalic acids.

As has been pointed out by Freundlich and Heller (*J. Amer. Chem. Soc.*, 1939, **61**, 2228) a factor of great importance in adsorption is the solvent. Thus, Jermolenko and Ginsberg (*Kolloid Shurn.*, 1939, **5**, 263) found that chloracetic acids from aqueous solutions were adsorbed on charcoal in the order: mono > di > tri, whilst in benzene or alcohol, the adsorption was exactly in the reverse order (*cf.* Sata and Kurano, *Kolloid Z.*, 1932, **60**, 137). That adsorption depends upon the nature of the solvent is also shown by the work of Bhatnagar, Kapur, and Bhatnagar (*J. Indian Chem. Soc.*, 1940, **17**, 361). These authors found that the adsorption from aqueous solutions of aliphatic acids by acid-condensed phenolic resins increased with increasing molecular weight, but the behaviour was reversed in the case of non-polar solvents. Adsorption by amino- and protein-resins was found to increase on the introduction of polar groups in the acid molecule. Thus, even with the same adsorbent, a comparison of adsorbability can only be permissible when the solvent is also the same (*cf.* also Cook, *J. Chem. Soc.*, 1938, 633; Zechmeister and Jorgens, *Naturwiss.*, **26**, 495; Elder and Springer, *J. Phys. Chem.*, 1940, **44**, 943).

In a previous paper (*J. Indian Chem Soc.*, 1942, **19**, 453), the adsorption of alkaloids from alcoholic solutions on active silica gel was measured. It was found that molecules with similar structure have similar adsorption. With a view to further studying the relationship between constitution and adsorption on active silica gel, the adsorption of a large number of organic acids, and the effect of substitution of polar groups on adsorption, have been investigated in the present paper.

## EXPERIMENTAL

The adsorbent used in these experiments was activated silica gel. The gel was prepared in the laboratory according to Patricks' method from sodium silicate solutions and hydrochloric acid, and obtained in a perfectly transparent, granular form. The gel was washed with repeated changes of hot distilled water, till the washings were neutral and entirely free from chlorides. The gel was activated as described in the previous paper (*loc. cit.*).

Alcoholic solutions (75 c.c.) of different acids were treated in stoppered bottles with 10g. of the activated gel in each case. The amount of adsorption was determined by titration against *N*/100 solution of caustic potash before and after adsorption. A mixture of neutral red and methylene blue was used as the indicator. The bottles were occasionally shaken and left for 72 hours to attain equilibrium. The acid solutions used in these experiments are all *M*/100 in concentration, except where otherwise stated. The temperature was throughout 25°. The experimental results are recorded in Tables I to VI.

TABLE I

*Adsorption of monobasic acids from alcoholic solutions on silica gel*

| Acids. | Formula. | Initial conc. | Equil. conc. | Amount adsorbed | % Adsorption. | No. of C atoms in molecule. |
|---|---|---|---|---|---|---|
| Formic ... | $HCOOH$ | 10·0 | 0·8 | 9·2 | 92·0 | 1 |
| Acetic ... | $CH_3COOH$ | 10·0 | 4·0 | 6·0 | 60·0 | 2 |
| Propionic ... | $C_2H_5COOH$ | 11·2 | 5·0 | 6·2 | 55·4 | 3 |
| Butyric ... | $C_3H_7COOH$ | 10·8 | 5·1 | 5·7 | 52·8 | 4 |
| Valeric ... | $C_4H_9COOH$ | 11·2 | 5·0 | 6·2 | 55·4 | 5 |
| Caproic ... | $C_5H_{11}COOH$ | 11·2 | 5·1 | 6·1 | 55·3 | 6 |
| Pelargonic | $C_8H_{17}COOH$ | 11·2 | 5·0 | 6·2 | 55·4 | 9 |
| Undecylic... | $C_{10}H_{21}COOH$ | 9·8 | 4·2 | 5·6 | 57·1 | 11 |
| Lauric ... | $C_{11}H_{23}COOH$ | 10·0 | 4·1 | 5·9 | 59·0 | 12 |
| Myristic ... | $C_{13}H_{27}COOH$ | 10·0 | 4·1 | 5·9 | 59·0 | 14 |
| Palmitic | $C_{15}H_{31}COOH$ | 10·0 | 4·1 | 5·9 | 59·0 | 16 |
| Margaric ... | $C_{16}H_{33}COOH$ | 9·8 | 4·1 | 5·7 | 58·2 | 17 |
| Stearic ... | $C_{17}H_{35}COOH$ | 10·0 | 4·3 | 5·7 | 57·0 | 18 |

TABLE II

*Adsorption of dibasic acids from alcoholic solutions on silica gel*

| Acids. | Formula. | Initial conc. | Equil. conc. | Amount adsorbed. | % Adsorption. | No. of C atoms in molecule. |
|---|---|---|---|---|---|---|
| Oxalic .. | $COOH \cdot COOH$ | 21·6 | 3·6 | 18·0 | 83·3 | 2 |
| Malonic ... | $CH_2(COOH)_2$ | 20·0 | 3·8 | 16·2 | 81·0 | 3 |
| Succinic ... | $C_2H_4(COOH)_2$ | 20·6 | 8·2 | 12·4 | 60·2 | 4 |
| Glutaric .. | $C_3H_6(COOH)_2$ | 21·6 | 11·4 | 10·2 | 47·2 | 5 |
| Adipic .. | $C_4H_8(COOH)_2$ | 22·6 | 13·2 | 9·4 | 41·6 | 6 |
| Phthalic ... | $C_6H_4(COOH)_2$ | 22·2 | 6·2 | 16·0 | 72·1 | 8 |

### TABLE III

*Effect of substitution by hydroxyl groups on adsorption*

| Acid. | Formula. | Initial conc. | Equil. conc. | Amount adsorbed. | % Adsorption. | Diff. |
|---|---|---|---|---|---|---|
| Propionic | $C_2H_5COOH$ | 11·2 | 5·0 | 6·2 | 55·3 | 0·0 |
| Lactic | $C_2H_4(OH)\ COOH$ | 10·6 | 2·8 | 7·8 | 73·6 | 18·3 |
| Succinic | $C_2H_4(COOH)_2$ | 20·6 | 8·2 | 12·4 | 60·2 | 0·0 |
| Malic | $C_2H_3(OH)(COOH)_2$ | 21·2 | 7·6 | 13 6 | 64·2 | 4 0 |
| *r*-Tartaric | $C_2H_2(OH)_2(COOH)_2$ | 20·8 | 6·8 | 14·0 | 67·3 | 7·1 |
| Benzoic | $C_6H_5COOH$ | 11·0 | 5·6 | 5·4 | 49·1 | 0·0 |
| *m*-Hydroxybenzoic | $(OH)C_6H_4COOH$ | 10·4 | 4·6 | 5·8 | 55·8 | 6·7 |
| Salicylic | $(OH)C_6H_4COOH$ | 11·4 | 3·4 | 8·0 | 70·0 | 20·9 |
| Naphthoic | $C_{10}H_7COOH$ | 11·0 | 4·2 | 6·8 | 61·8 | 0·0 |
| 2(OH)Naphthoic | $C_{10}H_6(OH)COOH$ | 10·8 | 1·4 | 9·4 | 87·0 | 25·2 |
| Phenylacetic | $C_6H_5CH_2COOH$ | 11·0 | 4·4 | 6·6 | 60·0 | 0·0 |
| Mandelic | $C_6H_5CH(OH)COOH$ | 11·2 | 1·3 | 9·9 | 90·1 | 30·1 |

### TABLE IV

*Effect of substitution of different groups in acetic acid*

| Acids. | Formula. | Initial conc. | Equil. conc. | Amount adsorbed. | % Adsorption. | Diff. |
|---|---|---|---|---|---|---|
| Acetic | $CH_3COOH$ | 10·0 | 4·0 | 6·0 | 60·0 | 0·0 |
| Monochloracetic | $CH_2ClCOOH$ | 10·2 | 2·0 | 8 2 | 80·4 | 20·4 |
| Dichloracetic | $CHCl_2COOH$ | 10·2 | 0 9 | 9 3 | 91 2 | 31·2 |
| Trichloracetic | $CCl_3COOH$ | 10·4 | 0·2 | 10 2 | 98·1 | 38·1 |
| Tribromacetic | $CBr_3COOH$ | 10·2 | 0·0 | 10·2 | 100 0 | 40 0 |
| Phenylacetic | $C_6H_5CH_2COOH$ | 11·0 | 4·4 | 6·6 | 60·0 | 0 0 |
| Malonic | $COOH.CH_2COOH$ | 20·0 | 3·8 | 16·2 | 81·0 | 21·0 |
| Mandelic | $C_6H_5CH(OH)COOH$ | 11·2 | 1·3 | 9·9 | 90 1 | 30·1 |
| Propiolic | $CH\equiv C\ COOH$ | 10·6 | 0·8 | 9·8 | 92 5 | 32·5 |
| Propionic | $CH_3CH_2COOH$ | 11 2 | 5·0 | 6·2 | 55 3 | -4 7 |

### TABLE V

*Effect of substitution of different groups in benzoic and succinic acids*

**A.** Benzoic

| Acid. | Formula. | Initial conc. | Equil. conc. | Amount adsorbed. | % Adsorption | Diff. |
|---|---|---|---|---|---|---|
| Benzoic | $C_6H_5COOH$ | 11·0 | 5·6 | 5·4 | 49 1 | 0 0 |
| *o*-Chlorobenzoic | $C_6H_4Cl\ COOH$ | 8·9 | 2·6 | 6·3 | 70·8 | 21·7 |
| *p*-Chlorobenzoic | $C_6H_4Cl\ COOH$ | 9·0 | 2·9 | 6·1 | 67·7 | 18·6 |
| *o*-Bromobenzoic | $C_6H_4Br\ COOH$ | 10·8 | 3·0 | 7·8 | 72 2 | 23·1 |
| *m*-Bromobenzoic | $C_6H_4Br\ COOH$ | 10·8 | 3 0 | 7·8 | 72·2 | 23·1 |
| *o*-Nitrobenzoic | $C_6H_4NO_2\ COOH$ | 10·2 | 2·2 | 8·0 | 78·4 | 29·3 |
| *p*-Nitrobenzoic | $C_6H_4NC_2\ COOH$ | 10·4 | 2·8 | 7·6 | 73·1 | 24·0 |
| *m*-Nitrobenzoic | $C_6H_4NO_2\ COOH$ | 10·2 | 2·4 | 7·8 | 76·5 | 27·4 |
| *o*-Toluic | $CH_3C_6H_4\ COOH$ | 10·2 | 5·6 | 4·6 | 45·1 | —4·0 |
| *m*-Toluic | $CH_3C_6H_4\ COOH$ | 10·2 | 5·6 | 4·6 | 45·1 | —4·0 |
| *p*-Toluic | $CH_3C_6H_4\ COOH$ | 10·6 | 5·0 | 5·6 | 52·8 | 3·7 |
| *o*-Hydroxybenzoic | $(OH)C_6H_4COOH$ | 11·4 | 3·4 | 8·0 | 70·0 | 20·9 |
| *m*-Hydroxybenzoic | $(OH)C_6H_4COOH$ | 10·4 | 4·6 | 5·8 | 55·8 | 6 7 |
| Anthranilic | $NH_2C_6H_4\ COOH$ | 11·0 | 2·6 | 8·4 | 76·4 | 27·3 |

**B.** Succinic

| Acid. | Formula. | Initial conc. | Equil. conc. | Amount adsorbed | % Adsorption. | Diff. |
|---|---|---|---|---|---|---|
| Succinic | $C_2H_4(COOH)_2$ | 20·6 | 8·2 | 12·4 | 60·2 | 0 0 |
| Dibromosuccinic | $C_2HBr_2(COOH)_2$ | 21·0 | 10·0 | 11 0 | 52·4 | —7·8 |
| Malic | $C_2H_3(OH)(COOH)_2$ | 21·2 | 7·6 | 13·6 | 64 2 | 4·0 |
| *r*-Tartaric | $C_2H_2(OH)_2(COOH)_2$ | 20·8 | 6·8 | 14 0 | 67·3 | 7·1 |
| *l*-Tartaric | $C_2H_2(OH)_2(COOH)_2$ | 20·8 | 6·6 | 14·2 | 68·3 | 8·1 |
| Meso-tartaric | $C_2H_2(OH)_2(COOH)_2$ | 21·0 | 6·4 | 14·6 | 69·5 | 9·3 |
| Phthalic | $C_6H_4(COOH)_2$ | 22·2 | 6·2 | 16·0 | 72·1 | 11·9 |

## DISCUSSION

The adsorptions of organic compounds from aqueous solutions on active charcoal, have often been examined in relation to Traube's rule. Traube showed that with successive members in a homologous series, the concentrations have to be diminished about threefold, in order that the same lowering of surface tension may be produced with each addition of a $CH_2$ group. As the lowering of surface tension is intimately connected with adsorption, Traube's rule has been stated by Freundlich to denote that the adsorption of organic substances from aqueous solutions increases regularly as one ascends the homologous series (Freundlich, *Z. physikal. Chem.*, 1906, **57**, 385; "Colloid and Capillary Chemistry", 1926, p. 195). Freundlich verified the rule in the case of the first four members of the fatty acid series. Subsequent investigators have generally supported Freundlich's conclusions, though occasional divergences have been noticed. Thus Fromageot and Wurmser (*loc. cit.*) record an irregularity in adsorption with successive members of the fatty acid series. Schilow and Nekrassow (*loc. cit.*) observed that the increase in adsorption with the addition of each $CH_2$ group, attained a maximum value between the fifth and sixth member of the fatty acid series. Previous work had mostly been limited to the first four members of the fatty acids. Linner and Gortner (*loc. cit.*) have more recently examined the adsorption of a larger number of the fatty acid homologues and found that Traube's rule is followed better in the case of more dilute solutions.

In the present experiments the adsorption of 13 members of the fatty acid homologues by silica gel from alcoholic solutions, have been measured. The results are recorded in Table I. An examination of the data shows that formic acid gives an abnormally large adsorption of 92%. The other members of the homologous series from aeetic acid to stearic acid, all give adsorptions which lie between 52·8 and 60%. It is thus remarkable that as the number of carbon atoms in the molecule increases from 2 to 18, the percentage adsorption varies but slightly and may be considered to be roughly constant. This result is thus quite different from the adsorption on the surface of carbon, where adsorption increases with each successive member in accordance with Traube's rule. Traube's rule, however, has generally been applied to the case of aqueous solutions. As the change in surface tension in the case organic solvents is generally small (*cf.* Gilbert, *J Phys. Chem.*, 1927, **31**, 543), Traube's rule will not necessarily apply to adsorption from organic solvents. In the case of silica gel, however, considerable adsorptions have been observed from benzene, toluene, nitrobenzene and other organic solvents (Patrick and Jones, *J. Phys. Chem.*, 1925, **29**, 1). It is evident that in the case of organic solvents, the lowering of surface tension cannot be considered as the chief criterion of adsorbability and consequently Traube's rule will not apply.

In the case of adsorption by silica gel, the reverse of the effect required by Traube's rule has been observed by several investigators. Holmes and McKelvey found a reversal of Traube's rule in the case of the adsorption of fatty acids from toluene solutions (*ibid.*, 1928, **32**, 1522). Bartell and Fu (*J. Phys. Chem.*, 1929, **33**, 676) investigated the adsorption by silica gel both from aqueous and from carbon tetrachloride solutions. The adsorption from aqueous solutions was very slight. In the case of $CCl_4$ solutions, they found a similar reversal of Traube's rule : the adsorption of the first four members of the fatty acids, decreased as one ascended the series. Apart from this reversal effect, if one compares the results of Bartell and Fu with the observations of Freundlich on adsorption from aqueous solutions by blood charcoal, one finds that the values of $a_{n+1}/a_n$, the ratio between the adsorption of successive members, is generally much higher in the case of charcoal than in the case of silica gel. In the following table, some of the data for the two adsorbents with different solvents, are given for comparison.

TABLE VI

| Acids. | Adsorption on blood charcoal from aqueous solutions (Freundlich). | | Adsorption on silica gel from $CCl_4$ solutions (Bartell and Fu). | | | |
|---|---|---|---|---|---|---|
| | Conc. | $a_{n+1}/a_n$. | Conc. | $a_{n+1}/a_n$. | Conc | $C_{n+1}/a_n$ |
| Formic ... | 0·10$N$ | — | 0·10$N$ | — | 0·02$N$ | — |
| Acetic ... | 0·10 | 1·26 | 0·10 | 0·856 | 0·02 | 0·879 |
| Propionic ... | 0·10 | 1·55 | 0·10 | 0·879 | 0·02 | 0·911 |
| Butyric ... | 0·10 | 1·56 | 0·10 | 0·904 | 0·02 | 0·929 |

As is clearly seen from the above table, in the case of adsorption from aqueous solutions on charcoal, the increase between successive members is about 55%, whilst in the case of $CCl_4$ solutions on silica gel, there is a mean decrease which is only about 12%, the solution in both the cases being $M/10$. With a more dilute $CCl_4$ solution, $M/50$, the difference in the adsorption of successive members is further reduced to 9·4%. From Bartell and Fu's data, it thus appears, that in dilute solutions the adsorption by silica gel from organic solvents, tends to become more or less comparable from member to member in the homologous series. This is in accordance with the observations recorded in the present experiments, with alcoholic solutions. It would be relevant to mention that in the case of aqueous solutions the adsorptions of successive members presist in showing a very marked increase even at a concentration of $M/100$ (*cf.* Schilow and Nekrassow *loc. cit*).

So far as the present experiments go, it might be considered that the adsorption of the fatty acid homologues on silica gel is independent of the length of the carbon chain (see Table I). This result can be explained if we consider that the adsorbed molecules are definitely oriented. The structure may be considered akin to that given by Langmuir for fatty acid films on water (*J. Amer. Chem. Soc.*, 1917, 1848). The carboxyl group, which is the active group of the fatty acid molecule, will be directed towards the surface of the adsorbent and the saturated $CH_3$ group will form the outermost layer. The adsorbed molecules will thus be more or less with their lengths at right angles to the surface. Such an oriented structure will give the same adsorption for all members of the fatty acid series irrespective of the length of the carbon chain. The amount of adsorption in every case will depend upon the area covered by the carboxyl group and the area in the case of all monobasic fatty acids will be the same. Although the above represents the structure of the adsorbed layer in a general way, a certain distortion in the orientation will set in owing to the presence of a polar group in the solvent itself.

TABLE VII

| Acid. | Formula. | $M/20$ soln. | | | | $M/10$ soln.* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $C_1$. | $C_e$. | $a$. | %ads. | $C_1$ | $C_e$. | $a$ | %ads. |
| Oxalic | $(COOH)_2$ | 9·6 | 6·1 | 3·5 | 30·2 | 20·4 | 16·2 | 4·2 | 25·9 |
| Malonic | $CH_2(COOH)_2$ | 9·6 | 8·6 | 1·0 | 10·6 | 20·0 | 18·8 | 1·2 | 6·0 |
| Succinic | $C_2H_4(COOH)_2$ | 9·7 | 8·6 | 0·6 | 6·2 | 20·6 | 19·8 | 0·8 | 3·9 |
| Glutaric | $C_3H_6(COOH)_2$ | 9·7 | 9·1 | 0·6 | 6·2 | 20·6 | 19·8 | 0·8 | 3·9 |
| Adipic | $C_4H_8(COOH)_2$ | 9·7 | 9·1 | 0·6 | 6·2 | 20·8 | 20·0 | 0·8 | 3·9 |
| Phthalic | $C_6H_4(COOH)_2$ | 9·7 | 9·1 | 0·8 | 8·2 | 21·0 | 20·0 | 1·0 | 4·8 |

* 10 c.c. solution titrated against $N/10$-KOH.

### *Variation of Adsorption of Dibasic Acids with Concentration*

In Table II, the adsorptions of dibasic acids on silicia gel are recorded. It will be seen that the percentage adsorption in this series shows a regular decrease with increase in number of carbon atoms in the chain. The adsorptions of dibasic acids on active charcoal from aqueous solutions have been measured by several authors. Fromageot and Wurmser (*loc. cit.*) did not find any difference for oxalic and succinic acids. Schilow and Nekrassow (*loc. cit.*) on the other hand, found an increase in adsorption as the number of carbon atoms in the molecule increased. This was confirmed by Linner and Gortner (*loc. cit.*) for concentrations below 0·05$M$, but the values approached each other in the vicinity of this concentration, except for oxalic acid. The present results are thus the complete reversal of the above observations. If we multiply the adsorption coefficients by the number of carbon atoms contained in the molecule, we get the figures as shown in Table VIII.

TABLE VIII

| Acid | Adsorption coeff. | No of carbon atoms. | Product |
|---|---|---|---|
| Oxalic acid | 83·3 | 2 | 166·6 |
| Malonic acid | 81·0 | 3 | 243·0 |
| Succinic acid | 60·2 | 4 | 240·8 |
| Glutaric acid | 47·2 | 5 | 236·0 |
| Adipic acid | 41·6 | 6 | 249·6 |

TABLE IX

| Acid. | % Adsorption | Dissociation constant |
|---|---|---|
| Acetic | 60·0 | $1{\cdot}8 \times 10^{-5}$ |
| Monochloracetic | 80·4 | $1{\cdot}56 \times 10^{-3}$ |
| Dichloracetic | 91·2 | $5{\cdot}1 \times 10^{-2}$ |
| Trichloracetic | 98·1 | $3{\cdot}0 \times 10^{-1}$ |

Thus, (Table VIII) excluding the single case of oxalic acid, the product is a constant within 3% of the mean value, 242·4. This strongly suggests that the orientation of the adsorbed molecules is such that they lie flat on the surface of the adsorbent. In other words, both the carboxyl groups now lie on the surface, and as one ascends the homologous series, the introduction of a $CH_2$ group increases the distance between the two carboxyls. Thus with the increase in the number of carbon atoms in the molecule, the area of the surface covered by the molecule also increases proportionately. The percentage adsorption thus decreases in a regular manner with increase in the number of carbon atoms.

Changes in the orientation of adsorbed molecules with increasing concentrations have been observed in a few cases. Thus, from the measurement of surface potentials due to phenols adsorbed on the water-air interface (Adam, "Physics and Chemistry of Surface", 1938, p. 137) it has been concluded that as the space available for each molecule on the surface is decreased, it tends to take up an increasingly vertical position, whereas originally it was lying almost flat. The effect of concentration has also been noted by Linner and Gortner (*loc. cit.*). Thus in the present case it is to be expected that as the concentration of the dibasic acids is increased, there would not be enough space after a certain limit for every molecule to lie flat on the surface, and a vertical orientation with only one carboxyl on the surface may become compulsory. In such a case the structure of the adsorbed molecules will be the same as in the case of the monobasic acid series, and the differences from member to member should vanish. That this is actually the case is evident from Table VII, where the percentage adsorption between successive members of the dibasic acid series becomes comparable.

The effect of substitution of hydroxyl group in the molecule on adsorbability is recorded in Table III. The hydroxyl group always produces an increase in adsorptions, but this increase is not constant in all the cases, being only 4% in the case of malic acid and as much 30·1% in the case of mandelic acid. When another OH-group is introduced into malic acid the resulting tartaric acid shows a further increase of 3·1%. The results are exactly the the reverse of those of Schilow and Nekrassow (*loc. cit.*). It is further interesting to note that the largest increase in the present case *viz.*, in mandelic acid, corresponds to the largest decrease observed by the above-mentioned authors. In this respect the behaviour with silica gel is thus the reverse of what has been observed with charcoal.

Substitution of halogens in the molecule (Tables IV and V) also always leads to an increased adsorption with the single exception of dibromosuccinic acid. In the acetic acid molecule, adsorption increases as the number of halogens introduced is increased. This is in the same order as the dissociation constants (and hence strength) of the resulting acids, as will be apparent from the above table.

Effect of substitution of different groups and radicals in acetic, benzoic and succinic acid molecules are shown in Tables IV and V respectively. No further remarks are necessary. If may be said in general that introduction of an active group leads to enhanced adsorption. Positional isomers as a rule do not differ much in their adsorbability, as also is the case with the few optical isomers studied.

Further work with different solvents is in progress.

In conclusion we must record our thanks to the Patna University for the grant of a research scholarship to one of us (B.P.G.).

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# SYNTHESIS OF COUMARINS FROM *o*-HYDROXY-ARYL ALKYL KETONES. PART IV. FORMATION OF *o*-COUMARIC ACIDS FROM *o*-HYDROXY-ALDEHYDES

BY DUHKHAHARAN CHAKRAVARTI AND SYED ABDUL MOMEN

2-Methoxy-5-methylbenzaldehyde, 2 : 4-dimethoxybenzaldehyde and 2-naphthol methyl ether-1-aldehyde have been condensed under Reformatsky's condition with ethyl bromoacetate and ethyl α-bromopropionate to give hydroxy-esters, which on dehydration and hydrolysis yield *trans*-acids (*o*-coumaric acids). It has been shown that 1-methoxy-aldehydes always lead to *trans-o*-methoxycinnamic acids by Perkin's reaction, by Chakravarti and Majumdar's method and by malonic acid condensation.

The *o*-hydroxy-aryl alkyl ketones have been conveniently used by Chakravarti *et al* (*J. Indian Chem. Soc.*, 1938, **15**, 136 ; 1940, **17**, 65) for the synthesis of coumarin derivatives.

In attempting to synthesise coumarin derivatives by this method, Chakravarti and Majumdar (*J. Indian Chem. Soc.*, 1939, **16**, 389) have observed that when *o*-hydroxy-aldehydes are condensed with ethyl bromoacetate or ethyl α-bromopropionate *trans*-cinnamic esters are formed, which do not yield coumarins on heating with hydriodic acid or on keeping with concentrated sulphuric acid in the cold as in the case of the cinnamic esters, obtained from *o*-hydroxy-aryl alkyl ketones.

The present investigation has been undertaken to study the general applicability of this method for the synthesis of *o*-coumaric acids by the condensation of the methoxy-aldehydes with ethyl bromoacetate and ethyl α-bromopropionate and subsequent dehydration and hydrolysis and to note the influence of any group in the phenyl nucleus on the formation of *o*-coumaric acids.

The following condensations have been studied and the products in each case have been found to be *trans*-cinnamic esters, which resist all attempts for lactonisation to coumarins.

| Aldehyde. | Halogenated fatty ester. | Product. |
|---|---|---|
| 2-Methoxy-5-methylbenzaldehyde | Ethyl bromoacetate | 2- Methoxy-5-methyl-*trans*-cinnamic acid |
| ,, | Ethyl α-bromopropionate | 2-Methoxy-5-methyl-*trans*-α-methylcinnamic acid |
| 2 : 4-Dimethoxy-benzaldehyde | Ethyl α-bromopiopionate | 2 : 4-Dimethoxy-*trans*-α-methylcinnamic acid |
| 2-Naphthol methyl ether-1-aldehyde | Ethyl bromoacetate | β-(2-Methoxy)-1-naphthylacrylic acid |
| ,, | Ethyl α-bromopropionate | β-(2-Methoxy)-1-naphthyl-α-methylacrylic acid |

The study of the condensation of 2-methoxy-aldehydes with ethyl bromoacetate and ethyl α-bromopropionate shows that the method of Chakravarti and Majumdar for the synthesis of *o*-coumaric acid seems to be a very general method as it is found that *trans*-esters are invariably formed if there is no β-alkyl substituent in the expected cinnamic ester.

A reference to literature shows that the methoxylated *o*-coumaric acids, preparad by this method, are identical with the *o*-methoxycinnamic acids, prepared by Perkin's reaction on 2-methoxy-aldehydes, *e.g.*, 2 : 4-dimethoxy-*trans*-cinnamic acid, prepared by the condensation of 2 : 4-dimethoxybenzaldehyde with ethyl bromoacetate, is identical with the acid described by Perkin and Schiess (*J. Chem. Soc.*, 1904, **85**, 162 ; Tiemann and Will, *Ber.*, 1882, **15**, 2079) ; *trans*-2-methoxy-α-methylcinnamic acid, prepared by the condensation of 2-methoxybenzaldehyde with ethyl α-bromopropionate, is identical with the acid prepared by Perkin (*J. Chem. Soc.*, 1877, **31**, 415).

In order to see whether Perkin's reaction on 2-methoxy-aldehydes always lead to the *trans*-acids and not the *cis*-acids, the aldehydes, *e.g.*, 2-methoxy-5-methylbenzaldehyde, 2 : 4-dimethoxybenzaldehyde, 2-naphthol methyl ether-1-aldehyde have been submitted to Perkin's reaction with acetic anhydride and sodium acetate and also with propionic anhydride and sodium propionate and in each case it has been found that the acids obtained are identical with the *trans*-methoxycinnamic acids, prepared by the condensation of the corresponding aldehydes with ethyl bromoacetate or ethyl α-bromopropionate.

The formation of *o*-coumaric acid thus seems to be characteristic of the 2-methoxy-aldehydes irrespective of any substituent in the phenyl nucleus. This has been further confirmed by studying the condensation of 2 : 4-dimethoxybenzaldehyde with malonic acid which also leads to the *trans*-acid (m.p. 184°, mixed m.p. 184°).

## EXPERIMENTAL

*Ethyl β-Hydroxy-β-(2-methoxy-5-methyl)phenylpropionate.*—A mixture of 2-methoxy-5-methylbenzaldehyde (8 g.), ethyl bromoacetate (13·4 g.), zinc wool (5·5 g.) and dry benzene (75 c.c.) was heated on a water-bath for 2½ hours when the zinc dissolved. The solution was poured into ice-cold dilute sulphuric acid, the benzene layer separated, washed with sodium carbonate solution and then with water and dried. On removing benzene it was distilled at 200°/12 mm. as a colourless oil, yield 5·5 g.

*Ethyt 2-Methoxy-5-methyl-*trans-*cinnamate.*—The above compound (5·5 g.) was converted into the unsaturated ester with thionyl chloride (3 g.) in presence of pyridine (3 g.) in dry ethereal solution (100 c.c.). The ethereal layer after decomposition of the excess of thionyl chloride with powdered ice, was washed with dilute hydrochloric acid, sodium carbonate and finally with water. On removing ether the product was distilled at 165°/7 mm., yield 3·8 g. (Found: C, 71·4; H, 7·4. $C_{13}H_{16}O_3$ requires C, 71·0; H, 7·27 per cent).

*2-Methoxy-5-methyl-*trans-*cinnamic Acid.*—(*a*) The above unsaturated ester (1 g.) was hydrolysed by means of alcoholic potassium hydroxide. The acid was crystallised from dilute alcohol, m.p. 145-46°. (Found: C, 68·7; H, 6·3. $C_{11}H_{12}O_3$ requires C, 69·2; H, 6·7 per cent).

(*b*) *By Perkin's reaction.*—2-Methoxy-5-methylbenzaldehydehyde (1 g.) was heated with acetic anhydride (2 g.) and fused sodium acetate (8 g.) at 180° for 10 hours. Dilute alkali was added to the mixture and the filtered solution acidified by hydrochloric acid, when the acid separated out which was crystallised from dilute alcohol, yield 7 g., m.p. 144-45° (mixed m.p. with the compound prepared above).

*Demethylation of Ethyl 2-Methoxy-5-methyl-*trans-*cinnamate and 2-Methoxy-5-methylcinnamic Acid.*—The ester or the acid was heated with hydriodic acid (sp. gr. 1·7) on a glycerine bath at 140° for 2 hours. The mixture was treated with powdered ice and then with ether. The ethereal solution was washed with cold dilute sodium carbonate solution. The ethereal solution was then kept for some time with cold dilute alkali and then washed with water. The ether was evaporated off, when there was no residue. The sodium carbonate and alkali washings on acidification gave a sticky precipitate, which, however, could not be crystallised.

The other compounds have been prepared in a similar manner and are described in Table I.

TABLE I

| Name of the compound. | Prepared from | Molecular formula. | M.p. or b.p. | Analysis Found C, | Analysis Found H, | Analysis Calc. C, | Analysis Calc. H, | Remarks. |
|---|---|---|---|---|---|---|---|---|
| (1) Ethyl α-methyl-2-methoxy-5-methylcinnamate | 2-Methoxy - 5 - methylbenzaldehyde+ethyl bromoacetate+zinc wool and the resulting hydroxy ester dehydrated with $SOCl_2$+pyridine | $C_{14}H_{18}O_3$ | B.p. 160°/5 mm. | 71 83 | 7·92 | 71·79 | 7·69 | Colourless liquid |
| (2) α-Methyl-2-methoxy-5-methyl-*trans*-cinnamic acid | Hydrolysis of (1) | $C_{12}H_{14}O_3$ | M.p. 109-10° | 70·0 | 6·8 | 70 65 | 7·4 | Crystallised from spirit |
| ,, | 2-Methoxy 5 methylbenzaldehyde+sodium propionate and propionic anhydride (Perkin's reaction) | | M p. 109-10° (mixed m p ) | | | | | |
| (3) Ethyl 2 :4-dimethoxycinnamate | 2 : 4 - Dimethoxybenzaldehyde+ethyl bromoacetate and the hydroxy-ester dehydrated with $SOCl_2$ + pyridine. | .. | B.p 160°/6 mm | | | | | Brown viscous liquid (*cf* Chakravarti and Majumdar, *J. Indian Chem. Soc.*, 1940, **18**, 390) |
| (4) 2 :4-Dimethoxy-*trans*-cinnamic acid | Hydrolysis of (3) | ... | M.p. 184° | ... | | | | ... |
| ,, | Perkin's reaction from 2 4-dimethoxybenzaldehyde- | | ,, | | | | | |
| ,, | 2 : 4 - Dimethoxybenzaldehyde + malonic acid + piperidine | | ,, | | | | | |
| (5) Ethyl . 2 :4-dimethoxy-α-methylcinnamate | 2 . 4 - Dimethoxybenzaldehyde + ethyl α-bromopropionate and the hydroxy-ester dehydrated with $SOCl_2$ + pyridine | $C_{14}H_{18}O_4$ | B.p. 200°/6 mm. | 67·5 | 7·26 | 67 2 | 7·2 | Viscous brown liquid |
| (6) 2 :4-Dimethoxy-α-methyl-*trans*-cinnamic acid | Hydrolysis of (5) | $C_{12}H_{14}O_4$ | M.p. 130° | 65 0 | 6·1 | 64 86 | 6·3 | Crystallise d from alcohol |
| ,, | 2 · 4 - Dimethoxybenzaldehyde + sodium propionate+propionic anhydride (Perkin's reaction) | | M.p. 130° (mixed m.p.) | | | | | |
| (7) Ethyl β-(2-methoxy)-1-naphthyl acrylate | 2-Naphthol methyl ether -1-aldehyde+ethyl bromoacetate and the hydroxy-ester dehydrated | $C_{16}H_{16}O_3$ | B.p. 210-12°/ 4 mm. | 75·5 | 6·5 | 75·0 | 6·3 | ... |
| (8) β-(2-Methoxy)-1-naphthyl acrylic acid | Hydrolysis of (7) | $C_{14}H_{12}O_3$ | M.p. 153-54° | 74·2 | 5·7 | 73·7 | 5·3 | ,, |
| ,, | 2-Naphthol methyl ether-1-aldehyde + sodium acetate + acetic anhydride (Perkin's reaction) | | M.p. 153° (mixed m p ) | | | | | |
| (9) Ethyl α-methyl-β-(2 methoxy-) 1-naphthyl acrylate | 2-Naphthol methyl ether-1-aldehyde + ethyl α bromopropionate and the hydroxy-ester dehydrated | $C_{17}H_{18}O_3$ | B.p. 220-25°/ 5 mm. | 75·8 | 6·6 | 75·5 | 6·6 | Viscous brown liquid |
| (10) α-Methyl-β-(2-methoxy-) -1-naphthyl acrylic acid | Hydrolysis of (9) | $C_{15}H_{14}O_3$ | M.p. 138-139° | 74 0 | 5·9 | 74·39 | 5·8 | Crystallised from alcohol |
| ,, | 2-Naphthol methyl ether 1-aldehyde+sodium propionate + propionic anhydride (Perkin's reaction) | | M.p. 138-39° (mixed m.p.) | | | | | |

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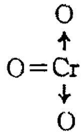
# PARACHOR OF CHROMIUM TRIOXIDE IN WATER

By P. M. Toshniwal, V. A. Moghe and W. V. Bhagwat

The experimental value of parachor of $CrO_3$ supports the view that ionic parachors are smaller than atomic parachors and $CrO_3$ ionises in water by forming either chromic or dichromic acid.

In our previous papers (*J. Indian Chem. Soc.*, 1942, **19**, 225, 492) we have shown that the parachors as determined by solution method will give correct value only if ionic and atomic parachors of elements are the same. The actual experimental work shows that they should be different. The works of Lakhani and Daroga (*ibid.*, 1938, **15**, 37, 320) and of Ray (*ibid.*, 1938, **15**, 43) support our view. We have extended this work to chromium trioxide in aqueous solutions. The constitution of chromium trioxide on the basis of electronic theory of valency is represented as  $O=\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{Cr}}$ or there is one double bond and two semipolar bonds. Hence the parachor of $CrO_3 = P_{Cr} + 3P_o + P_{\text{double bond}} + 2P_{\text{semipolar bond}} = 54 + 60 + 23{\cdot}2 - 3{\cdot}2 = 134$.

The actual value obtained by us is in the neighbourhood of 103. This low value clearly indicates that $CrO_3$ exists in solution in ionic form by combining with water and forming $H_2CrO_4$ or $H_2Cr_2O_7$. The lower value obtained by experiment is in agreement with the view that ionic parachors are smaller than atomic parachors for the same element. Similar considerations with $H_2Cr_2O_7$ support the fact that $CrO_3$ ionises in solution. Results are given in the tables below :

where $\gamma$ = Surface tension of the solution. $P_m$ = Parachor of the mixture. $P_x$ = Parachor of the solute. $X$ = molar fraction of the solute. $d$ = Density of the mixture.

### *Parachor of Chromium Trioxide*

The results of parachor of chromium trioxide at different concentrations in aqueous solution ($P_{\text{water}} = 52{\cdot}6$) are recorded below :

TABLE I

| | $x_{(CrO_3)} = 0{\cdot}15139$ | | | | $x_{(CrO_3)} = 0{\cdot}13263$ | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. | Density. | $\gamma$. | $P_m$. | $P_x$. | Density. | $\gamma$. | $P_m$. | $P_x$. |
| 20° | 1·488 | 72·01 | 59·61 | 102·4 | 1·424 | 71·34 | 58·72 | 102·7 |
| 30 | 1·484 | 71·71 | 59·89 | 104·1 | 1·415 | 71·03 | 59·05 | 105·1 |
| 40 | 1·478 | 71·44 | 60·26 | 106·2 | 1·408 | 70·50 | 59·13 | 105·8 |
| 50 | 1·470 | 70·84 | 60·40 | 107·6 | 1·402 | 69·58 | 59·32 | 107·2 |

TABLE II

| | $x_{(CrO_3)} = 0{\cdot}100928$ | | | | $x_{(CrO_3)} = 0{\cdot}11727$ | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. | Density. | $\gamma$. | $P_m$. | $P_x$. | Density. | $\gamma$. | $P_m$. | $P_x$. |
| 20° | 1·361 | 69·98 | 57·28 | 100·3 | 1·380 | 70·52 | 57·98 | 103·0 |
| 30 | 1·353 | 69·36 | 57·51 | 102·4 | 1·373 | 70·33 | 58·26 | 105·4 |
| 40 | 1·346 | 69·04 | 57·76 | 104·6 | 1·366 | 70·11 | 58·41 | 107·2 |
| 50 | 1·337 | 68·68 | 58·05 | 107·3 | 1·359 | 69·81 | 58·59 | 107·9 |

### TABLE III

| | $x_{(\mathrm{cro_3})}=0·095103$ | | | | $x_{(\mathrm{cro_3})}=0·02940$ | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. | Density. | $\gamma$. | $P_m$. | $P_x$. | Density. | $\gamma$. | $P_m$. | $P_x$. |
| 20° | 1·320 | 70·74 | 56·67 | 104·6 | 1·111 | 72·24 | 53·10 | 103·4 |
| 30 | 1·313 | 70·25 | 56·89 | 104·8 | 1·105 | 70·81 | 53·14 | 105·7 |
| 40 | 1·309 | 69·60 | 56·96 | 105·0 | 1·101 | 69·72 | 53·18 | 105·9 |
| 50 | 1·302 | 69·08 | 57·15 | 106·1 | | | | |

### TABLE IV

| | $x_{(\mathrm{cro_3})}=0·05666$ | | | | $x_{(\mathrm{oro_3})}=0·1538$ | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. | Density. | $\gamma$. | $P_m$. | $P_x$. | Density. | $\gamma$. | $P_m$. | $P_x$. |
| 21° | 1·200 | 71·61 | 54·89 | 101 4 | 1·491 | 73·81 | 60·19 | 104·6 |
| 30 | 1·196 | 71·06 | 54·94 | 102·3 | 1·483 | 73·40 | 60·43 | 106·2 |
| 40 | 1·190 | 69·44 | 54·93 | 102·3 | 1·474 | 72·88 | 60·68 | 107·8 |
| 50 | 1·185 | 68·45 | 54·95 | 102·5 | 1·465 | 72·16 | 60·91 | 109·2 |

### TABLE V

| | $x_{(\mathrm{cro_3})}=0·08078$ | | | | $x_{(\mathrm{cro_3})}=0·06904$ | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. | Density. | $\gamma$. | $P_m$. | $P_x$. | Density. | $\gamma$. | $P_m$. | $P_x$. |
| 20° | 1·277 | 71·42 | 56·10 | 101·5 | 1·243 | 71·76 | 55·44 | 100·5 |
| 30 | 1·270 | 70·87 | 56·13 | 102·0 | 1·237 | 70·78 | 55 48 | 101·1 |
| 40 | 1·262 | 70·05 | 56·42 | 105·1 | 1·229 | 68·96 | 55·46 | 100 8 |
| 50 | 1·260 | 68·17 | 56·15 | 102·1 | 1·224 | 67·76 | 55·46 | 100·8 |

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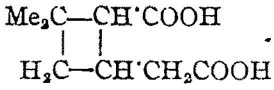
# EXPERIMENTS ON THE SYNTHESIS OF CARYOPHYLLENIC ACID

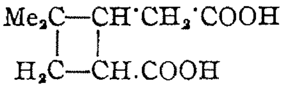
By M. D. Owen

A partial synthesis of caryophyllenic acid from dimethylketene and *cyclo*pentadiene is described along with a suggestion as to how the final stage in the synthesis may be carried out.

Caryophyllenic acid (I) or (II) is produced during the degradation, in stages, of $\beta$-caryophyllene and the elucidation of the structure of caryophyllenic acid would provide valuable information in establishing the structure of $\beta$-caryophyllene (Ramage and Simonsen, *J. Chem. Soc.*, 1938, 1208). Rydon (*Chem. Ind.*, 1938, **57**, 123) on the assumption that caryophyllenic acid is 2-carboxy-3:3 dimethyl*cyclo*butylacetic acid (I), has suggested that Ruzicka's formulae (III) or (IV) should be replaced by (V) or (VI). However, Ramage and Simonsen (*Chem. Ind.*, 1939, **58**, 447), have produced evidence which shows that Rydon's formulæ are untenable.



(I)



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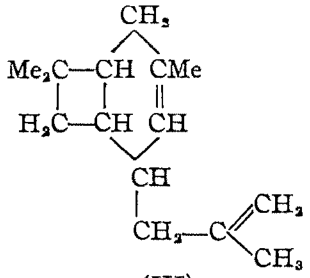
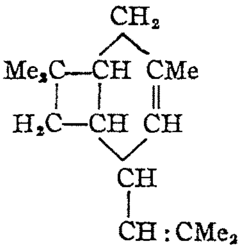
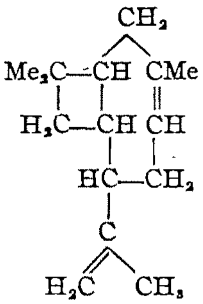


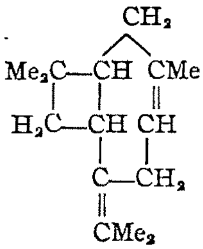
(III)



(IV)



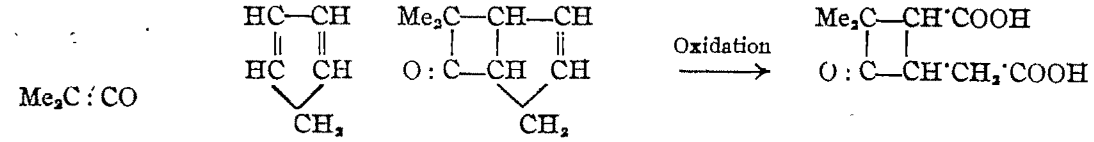
(V)



(VI)

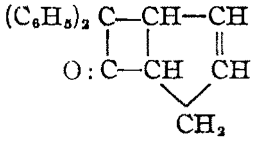
The writer, in collaboration with Dr. G. R. Ramage and Prof. J. L. Simonsen, was engaged on the synthesis of caryophyllenic acid from dimethylketene and *cyclo*pentadiene when the outbreak of war interfered with the research and it is desired to record, in brief, the progress that was made.

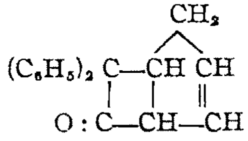
The following scheme represents the series of reactions which were carried out successfully :—



Dimethylketene *cyclo*Pentadiene (VII) (VIII)

It has been shown by Lewis, Ramage and Simonsen (*J. Chem. Soc.* 1937, 1837) that diphenylketene condenses with *cyclc*pentadiene to form the unsaturated dicyclic ketone (IX) and not (X)


(IX)


(X)

Arguing by analogy it is probable that dimethylketene will give (VII) and the latter will, on oxidation, give 2-carboxy-3:3-dimethyl*cyclo*butanone-acetic acid. Efforts to reduce this acid to caryophyllenic acid (I) by the usual methods were not successful, the alcohol being generally formed. There were, however, indications of success when sodium amalgam was used.

Other methods of synthesis have also been tried by Owen, Ramage and Simonsen (*J. Chem. Soc.* 1938, 1211) and the method described above has been extended by condensing dimethylketene with *cyclo*hexadiene to produce the homologue of caryophyllenic acid. It is hoped to complete and publish this work in detail at a more favourable time.

## EXPERIMENTAL

Dimethylketene was prepared from dimethylmalonic acid using the method described by Staudinger (*Helv. Chim. Acta*, 1925, **8**, 306) and *cyclo*pentadiene was distilled from a mixture of its polymers using a pear fractionating column at least one foot high. Slightly more than the theoretical amount of the freshly distilled *cyclo*pentadiene was added to the dimethylketene, the latter being contained in its receiver surrounded by a freezing mixture of solid carbon dioxide and ether. In about 12 hours the mixture became colourless and the pronounced camphoraceous odour of the dicyclic ketone was noticed, the yield being nearly theoretical. The ketone was distilled slowly two or three times through an air condenser to remove most of the excess of *cyclo*pentadiene and it was then purified through its semicarbazone. [The yield of the keto-acid (VIII) was much reduced when the ketone was not carefully purified before oxidation.]

The dicyclic ketone was then stirred with acetone in a three-necked flask surrounded by ice and containing a thermometer and stirrer. Finely ground potassium permanganate was added in small portions over a period of about 8 hours whilst the temperature inside was not allowed to rise above 4°. At the end of this period, the acetone was removed, water was added and sulphur dioxide bubbled through until the manganese oxide had gone into solution. The acid was thoroughly extracted with ether, the extract shaken several times with sodium carbonate solution, separated, acidified, and again thoroughly extracted with ether. The m.p. of the acid was found to be 124-25°.

The above work was carried out under the direction of Prof. J. L. Simonsen and Dr. G. R. Ramage.

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# CHEMICAL ACTIVITY OF HALOGEN DERIVATIVES OF SUBSTITUTED AMIDES OF MALONIC ACID. PART I. INTERACTION OF GRIGNARD'S REAGENT ON THE CHLORO DERIVATIVES OF SUBSTITUTED AMIDES OF MALONIC ACID

By K. G. Naik, R. K. Trivedi and S. M. Mehta

The following dichloro derivatives of the substituted amides of malonic acid have been interacted with the Grignard's reagent *viz.* phenyl magnesium bromide and benzyl magnesium chloride.

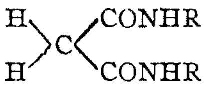
(1) Dichloromalondiphenylamide. (2) Dichloromalondi-*p*-tolylamide. (3) Dichloromalondi-*o*-tolylamide (4) Dichloromalondi-1:3:4-xylylamide.

Contrary to expectations, instead of ditertiary alcohols, monochloro derivatives of the following type were obtained, from the above substances *viz.*

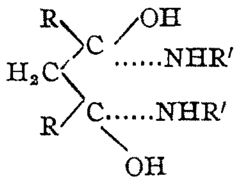
$(Cl)HC:(CONHR)_2$, where R may be phenyl, tolyl or xylyl group.

The investigations embodied herein were undertaken with a view to throwing some light on the interaction taking place between the Grignard reagent and the chloro derivatives of the substituted amides of malonic acid. In previous work attention was mainly concentrated upon the reactivity of the hydrogen atoms of the methylene group situated between two carbonyl groups. Other centres of activity of the molecules of such substances have not been investigated up to now.

From the inspection of a structure such as (I) it will be seen that there are at least three points of attack *viz.* :—



(I)



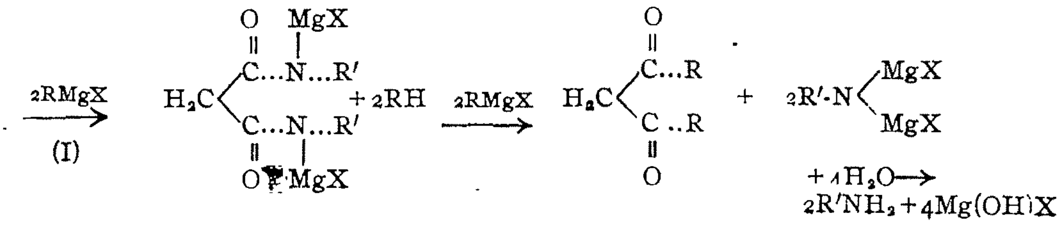
(II)

(*i*) the hydrogen atoms of the methylene group,

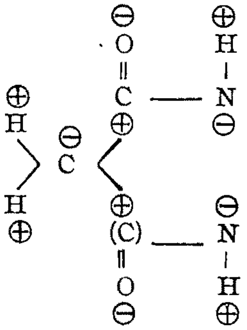
(*ii*) the hydrogen of the imino groups, and

(*iii*) the carbonyl groups.

It may be assumed that substances having the structure (I) would present to the Grignard reagent points of attack at the carbonyl (CO) as well as at the imino (-NH-) groups. In the event of the carbonyl group reacting the compound (II) would be formed and if imino groups react, the course of reaction would be anticipated as follows :—



It has been found, however, that unreacted amide is obtained when malondiphenylamide and malondibenzylamide are reacted with phenyl magnesium bromide. The explanation of this inactivity may be sought in the influence of -NHR- group in the case of the carbonyl groups and of (-R-) radicals in tha case of imino groups. According to the hypothesis of Vörlander, the atoms of a radical or those of a continuous system may exhibit an alternate polarity which may be symbolised by means of ⊕ and ⊖ signs, attached to the individual atoms. As such, the reacting amide may be represented as :—

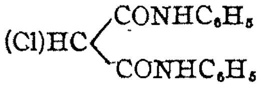


It will be seen from the above that the radicals ($C_6H_5$), which are positive as a whole, induce a greater charge of opposite sign on the nitrogen of the imino groups; this increased negative charge on the nitrogen holds very firmly the hydrogen atom which itself is positively charged as to keep it hooked with a greater force than before, with the result that the hydrogen is rendered unreplaceable by the reagent. Consequently, the imino (NH) group, as a whole, becomes inactive. Again, the negatively charged nitrogen induces a higher positive polarity on the carbon atom of the carbonyl group ; as a result, the negatively charged oxygen has to utilise all its negative polarity for being hooked on to the carbon atom with a greater force than before. It is, therefore, very unlikely that the oxygen atoms can possess any residual negative force which could induce the free valency of the fragment (-MgX) to attach to itself. This renders the carbonyl group also inactive towards the Grignard reagent.

The chloroderivatives of various amides of malonic acid are more reactive than the corresponding non-chlorinated substances and hence the following compounds have been selected for the investigation of their interaction with the Grignard's reagent.—

(*i*) Dichloromalondiphenylamide ;
(*ii*) Dichloromalondi-*p*-tolylamide ;
(*iii*) Dichloromalondi-*o*-tolylamide ;
(*iv*) Dichloromalondi-1 : 3 : 4 : 4-xylylamide.

Dichloromalondiphenylamide reacts vigorously with phenyl magnesium bromide yielding colourless product (III), m.p. 176°.



$$(Cl)HC\begin{cases} CONHC_6H_5 \\ CONHC_6H_5 \end{cases}$$

(III)

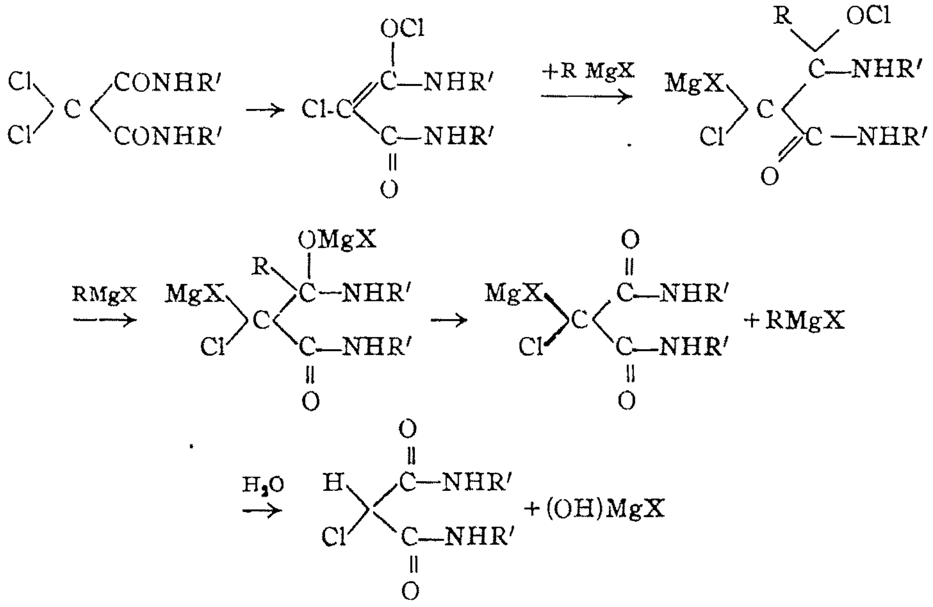
The reaction product has been assigned the formula (III) because

(*i*) The chlorine atom could be reduced quantitatively by hydriodic acid generated from KI and KCl (Kurt Meyer, *Annalen*, 1911, **380**, 212 ; *J. Chem. Soc.*, 1921, **119**, 951, 305).

(*ii*) On treatment of the product with sulphuryl chloride dichloromalondiphenylamide is obtained.

(*iii*) When the product is treated with aniline, it gives a product which is identical with the reaction product of monochloroethyl malonate and aniline.

The course of reaction can be explained by the following mechanism :



Such a mode of mechanism is not unusual in view of the fact that a similar reaction has been found to take place in the case of the semicarbzone of dimethylbutylacetophenone and Grignard's reagent (Biquard, *Bull. Soc. chim.*, 1938, **5**, 209).

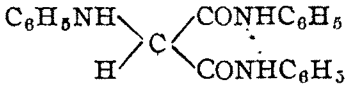
In attempting to knock off the second chlorine atom by using four molecules of the Grignard's reagent for every molecule of the dichloro derivative, it has been found out that the amide $H_2C : (CONHR')_2$ does not result but a very little quantity of the monochloro compound together with a large amount of uncrystallisable resinous mass is obtained.

The difference in the reactivity of the chlorine atoms in such dichloro derivatives is not unusual, as substantiated by the velocity of replacement of chlorine atom by hydrogen (*cf.* Part II of this series, *this issue*, p. 355).

The present investigation is of interest because some previous attempts made, as outlined under (*i*) and (*ii*) below, to obtain monochloro derivatives of the substituted amids of malonic acid did not give any conclusive results—

(*i*) The action of 1 molecule of sulphuryl chloride on the amide leads to a mixture of dichloro derivative and the original amide and not the monochloro compound.

(*ii*) Conrad and Bischoff tried to condense monochloro-ethyl malonate with aniline, probably in the hope of converting it into monochloromalondiphenylamide, but evidently they obtained the compound (IV).



$$\begin{matrix} C_6H_5NH \\ H \end{matrix} \!\!> C < \!\! \begin{matrix} CONHC_6H_5 \\ CONHC_6H_5 \end{matrix}$$

(IV)

Dichloromalondi-*p*-tolylamide, dichloromalondi-*o*-tolylamide and dichloromalondi-1:3:4-xylylamide have been reacted with phenyl magnesium bromide to give compounds of the type (III)

It also seems that the nature of the organic radical in the molecule of the Grignard reagent has no influence on the structure of the final product of reaction, for, when benzyl magnesium chloride is reacted with these substances, derivatives of the same type are obtained.

## EXPERIMENTAL

*The Interaction of Phenyl Magnesium Bromide with Dichloromalondiphenylamide.*—To a solution of phenyl magnesium bromide (2 mols.), prepared from magnesium turnings (2·4 g.) and dry bromobenzene (16·5 g.) in presence of dry ether dichloromalondiphenylamide (16 g.), disoslved in absolutely dry benzene, was gradually added. A white mass, slowly turning to brownish yellow, was found to separate immediately with the liberation of heat. When the addition was complete, the mixture was refluxed on a water-bath for about an hour to complete the reaction. When the flask attained the room temperature, 50 c.c. of 30% ice-cold hydrochloric acid were added slowly through the separating funnel and the mixture stirred vigorously for about 3 quarters of an hour. After transferring the contents into the single-necked flask, it was subjected to steam-distillation, in order to drive off benzene and other secondary volatile products like diphenyl etc., formed during the reaction. The brownish yellow mass, left behind, was filtered off, and washed with a little alcohol; it was then lixiviated with petroleum and crystallised from 50% alcohol. The pure chloromalondiphenylamide, thus obtained, was in the form of feathery needles, m.p. 176°.

It is fairly soluble in alcohol, acetone, ether, chloroform, acetic acid, pyridine, etc, but, sparingly soluble in benzene and practically insoluble in petroleum.

Other compounds were prepared in a similar way. The properties and analysis of all the compounds have been given in the following table :

| Name of the substance | M.p. | Crystalline structure. | Solubility. | Analysis. | |
|---|---|---|---|---|---|
| | | | | Found. | Calc. |
| Chloromalondiphenylamide.<br>$C_{15}H_{13}O_2N_2Cl$ | 176° | Feathery needles | Soluble in alcohol, acetone, ether, chloroform, pyridine. | Cl, 12 22% | Cl, 12 30% |
| Chloromalondi-*p*-tolyl amide.<br>$C_{17}H_{17}O_2N_2Cl$ | 212° | Shining colourless plates. | ,, | Cl, 11·05%<br>N, 8·93% | Cl, 11·21%<br>N, 8 85% |
| Chlcromalondi-*o*-tolyl amide.<br>$C_{17}H_{17}O_2N_2Cl$ | 179° | White microscopic crystals. | ,, | Cl, 11·24%<br>N, 9·02% | Cl, 11·21%<br>N, 8·85% |
| Chloromalondi-1:3:4-xylvlamide.<br>$C_{19}H_{21}O_2N_2Cl$ | 202° | White microscopic crystals. | ,, | Cl, 10·21%<br>N, 8·27% | Cl, 10 30%<br>N, 8·13% |

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# SPREADING OF LIQUIDS ON MERCURY SURFACE

By BHOLANATH GHOSH

The laws of spreading of water containing traces of HCl, $H_2SO_4$, $HNO_3$, $H_3PO_4$, NaCl, KCl, RbCl, CsCl, and colloidal graphite solution irradiated by X-rays have been studied on Hg surface, and the number of $H^+$ or alkali ions necessary to produce a critical area of $1 cm^2$. has been evaluated. The nature of the spreading forces, the significance of Harkin's coefficient controlling the spreading phenomenon have also been discussed.

The spreading of liquids and solutions on filter paper has been studied in detail by Prasad and the author in a series of papers (Prasad and Ghosh, *Kolloid Z.*, 1938, **84**, 275; 1937, **79**, 19; Ghosh, *Bull. Pat. Sc. Coll. Phil Soc.*, Jan. 1941. *cf.* Burdon, "Surface Tension and Spreading", p. 28). The mechansim of such spreading as controlled by adsorption has also been discussed therein. The structure of the solid, its field of force and free energy, besides the viscosity, surface tension and angle of contact of the liquid play important rôle in the spreading phenomena. For arriving at a relevant law of spreading the method of the Theory of Dimension was used. The spreading of one liquid A over another B belongs to an entirely different category, and demands a reduction of the free energy for the whole system for spreading to occur. For this the Harkin's coefficient ($S_{AB}$) must be positive,

$$S_{AB} = \gamma_B - \gamma_A - \gamma_{AB}$$

Here $\gamma_A$ and $\gamma_B$ are the surface tensions of the two liquids and $\gamma_{AB}$ is the interfacial tension between the two liquids. The corresponding energy condition for spreading of liquid A over solid B is

$$2\gamma_A < \gamma_A \ (1 + \cos\theta)$$

*i.e.* the adhesion of the liquid for the solid B must exceed the adhesion of the liquid itself. The condition for equilibrium of a liquid over a solid, exposing contact angle $\theta$ is

$$\gamma_B = \gamma_{AB} + \gamma_A \cos\theta.$$

Hence the previous equation. $\gamma_A \cos\theta$ is known as the adhesion tension of the liquid. This equation imposes an impossible condition for spreading, even when $\theta$ is 0. But experimentally we find that even an equivalence of the two sides of the formulae leads to spreading. Coming to the spreading of liquids on mercury, we find that for spreading to occur, in the case of non-spreading liquids, a minute quantity of an active substance, called promotor, is necessary. The action of the promotor is to change the nature of the surface over which the spreading is occurring by forming a monomolecular layer of some ion over the spreading surface. This reduces the value of $\gamma_{AB}$ and hence the spreading forces begin to preponderate over forces that try to keep the liquid collected in the form of a drop. In the case of spreading of water on mercury it is found that the addition of a minute quantity of acid or salt to water (about $10^{-6}$ g. of promoter per g. of water) is an important necessity for spreading. The author finds that salts of the alkali metals behave like acids but not to that degree of spreading efficiency. Traces of metallic hydroxides, however, stop spreading. It is to be mentioned here that irradiation of water, containing traces of colloidal gold or graphite, with X-rays also produces spreading even without addition of acids. Such irradiation effect in the case of spreading of heavy mineral oils is already known from the work of Stenstrom and Vigness (*J. Phys. Chem.*, 1939, **43**, 531) who find that illumination by ultraviolet light of wave-length less than 2800Å induces spreading power in oils, perhaps by making a small fraction of the molecules unsaturated.

Irradiation of light and heavy praffins by γ-rays, X-rays or ultra-violet light also produces similar effect (Allen, Grant and Burdon, *Trans. Faraday Soc.*, 1937, **33**, 153). The following are the laws for spreading of irradiated oils and paraffins on water (Stenstrom and Vigness, *loc. cit.*, p. 298; Landt and Volmer, *Z physikal. Chem.*, 1926, **122**, 398).

In the initial stage of spreading,

$\frac{da}{dt} \propto A$, where $A$ is the area of the drop at instant $T$, since spreading began. At a later stage, $A \propto t^4$.

It is well known that the presence of copper, gold and similar ions affects the laws of spreading profoundly (Meyers, and Harkins, *Nature*, 1937, **139**, 36; Mitchell, Rideal and Schulman, *ibid.* p. 625; Burdon, *Proc. Phys. Soc.*, 1926, **38**, 148).

It should be mentioned here that the quantity of these ions also, must be very minute. *i.e.* less than $10^{-6}$ g. per g. of water, otherwise the velocity of spreading will be too great for convenient observation.

The broad features of spreading of liquids on Hg consists of two parts *viz.*, (*a*) A very rapid spreading in the beginning, which can only be timed by special devices, and where spreading depends on the number of active ions, reaching the interface from the volume of the spreading liquid. Here the velocity of spreading is in general directly proportional to the radius of the liquid film (Burdon, Fuller and Gibson, *loc. cit.*) though wide departures from this law are also met with, in the case of some solutions which aspect will not be treated here. (*b*) A slower second stage, where the velocity of propagation of the liquid front is generally constant. The area covered by the liquid at the point where transition of laws takes place is found to be proportional to the volume of the drop at constant concentration of the acid. In order to obtain 1 sq. cm. value for this critical area a fixed volume of the liquid is necessary for each concentration of the acid. This volume is, however, inversely proportional to the concentration of the acid if the latter be varied. It can be easily calculated from the observed data obtained by previous workers that $10^{14}$ molecules of monobasic acids, organic or inorganic, are necessary for obtaining a critical area of 1 sq. cm. (Burdon and Oliphant, *Trans. Faraday Soc.*, 1927, **23**, 205). After the second stage, during which slow adsorption of the residual ions from the solution is taking place from areas previously covered as well as migration of ions from areas previously covered is occurring, a third stage sets in, where almost pure liquid is spreading. Here the velocity of spreading is decaying in an exponental manner. The intrinsic importance of the second critical area has not been worked out as yet.

## EXPERIMENTAL

Over the horizontal surface of mercury, parallel to it, and a few centimeters apart from it, a glass plate with two arrays of parallal straight lines, mutually perpendicular to one another, was placed. The glass plate had a central hole, through which the liquid could be poured over mercury. Photographs of the spreading liquid film were taken on a cinematograph film, moving at a known speed, with the help of a Cine camera, for studying the laws in the initial portion of spreading. The arrangment for photography and the method of dropping is the same as that adopted by Burdon and Oliphant (*loc. cit.*). For later stages, observations with a stop-watch could be conveniently taken. For the first stage some observations were also taken with stop-watches. In some cases by the application of a proper potential difference between Hg surface and the drop the latter could be held stationary and by opening the electric circuit the drop was allowed to spread. These types of electrically controlled spreading will be the subject matter of a subsequent paper. In some cases after the drop had spread up to a certain distance, the electric field between the spreading drop and Hg was put on in such a way that the drop began to contract and it came back gradually to its original radius. The lower branches of the curves (Fig. 2) reveal this contraction phenomenon, and the position at which the field is put on is marked with double arrow-heads.

For the direct determinations of the spreading pressure, the torsion balance used by Adams and his co-workers for studying force-area curves of films spread on water has been used by the present author.

For the spreading of weak acid solutions, conductivity water, either pure or contaminated with traces of colloidal metals and irradiated by X-rays, and electrolytic solutions of the alkali chlorides the following laws are valid.

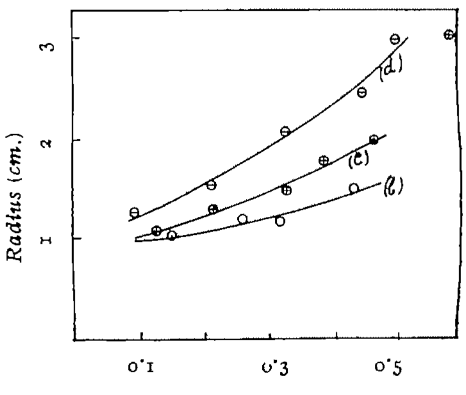
Stage 1, $V_1=K_1r$, where $K_1$ is constant ; Stage 2, $V_2=K_2$, where $K_2$ is another constant; Stage 3, $V_3=V_2e^{-\gamma(r-r_0)}$, where $r$ is the radius of spreading film at a point where $V_3$ is velocity, $\lambda$ is a constant and $r$, the value of the radius at which the second stage of spreading comes to an end. Many disturbing factors, however, vitiate spreading according to the third law.

Let $v$=volume of the drop in c.c., $x\,N$, the strength of the acid or salt solution in terms of normality $N$, and $r_1$, the radius at which the first break occurs, involving transition from law 1 to law 2, then it follows that in area $\pi r_1^2$, $\frac{vx.\,6{\cdot}06\times10^{23}}{\pi r_1^2\ 1000}$ ions had been adsorbed. From this we get the value of $p$ where

$$p=\frac{vx.\,6\ 06\times10^{23}}{\pi r_1^2.1000}.$$

$p$, denotes the number of equivalent monovalent ions necessary to produce 1 sq. cm. of critical area.

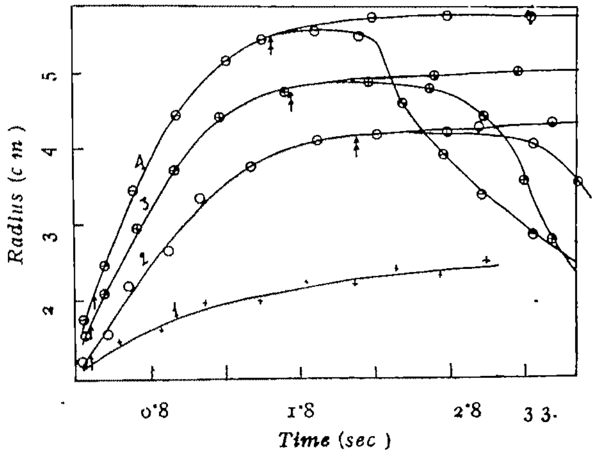
Fig. 1



Curves $b-d$ refer respectively to HCl soln of ''0·513 c.c vol. of conc $0{\cdot}2\times10^{-6}N$, HCl of 0 302 c.c. vol. of conc. $0{\cdot}5\times10^{-6}N$ and $HNO_3$ of 0·230 c.c. vol of conc. $1{\cdot}\times10^{-6}N$

Fig. 2

(2nd and subsequent stages)



Curves 1–4 refer respectively to

(1) Distilled water (vol. 0 421 c.c.)
(2) HCl soln. (*vide b* of fig. 1.
(3) ,, (*vide c* of fig. 1.
(4) $HNO_3$ (*vide d* of fig 1).

Spreading curves for a few typical cases are shown in Figs. 1, 2, 3. Fig. 1 represents the initial stage of spreading up to the first break. Fig. 2 depicts spreading from the onset of the first break up to the limiting range of spreading.

The values of *p*, calculated for different acids and salts, are given in Table II. The values of $K_1$ for the first stage of spreading are given in Table I for three typical observations. In Table IV the values of spreading pressure, interfacial tension between Hg and solution, as determined by the drop-weight method after using corrections given in International Critical Tables, and surface tension of Hg as measured by the author, are recorded.

Fig. 4

*Spreading of conductivity water* (vol. = 0·504 c.c.)

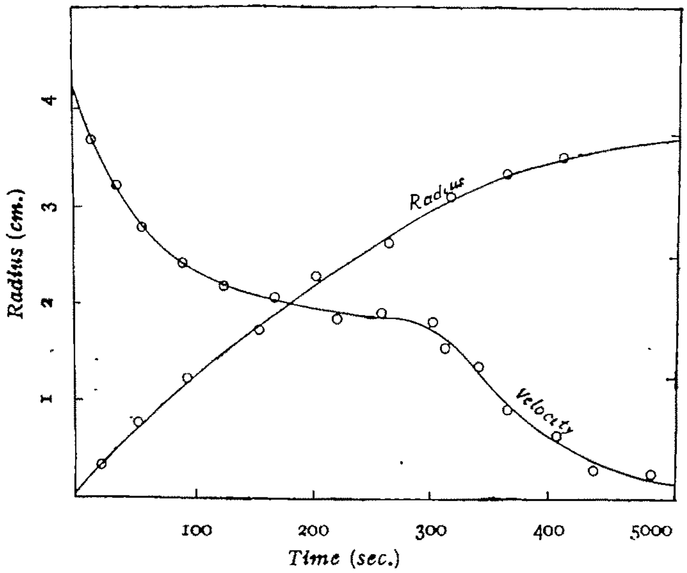


TABLE I

| Solution of | Vol. of drop. | Conc. solution. | Radius at which 1st break occurs. | Time at which 1st break occurs. | $k_1$. | $\nu k_1$. |
|---|---|---|---|---|---|---|
| HCl | 0·513 c.c. | $0{\cdot}2 \times 10^{-5}N$ | 1·401 cm. | 0·48 sec. | 0·7621 | 0·391 |
| HCl | 0·302 | $0{\cdot}5 \times 10^{-5}$ | 1·698 | 0·50 | 1·262 | 0·381 |
| $HNO_3$ | 0·230 | $1{\cdot}0 \times 10^{-5}$ | 2·096 | 0·52 | 1·842 | 0·424 |

TABLE II

*N* = Normality of acid in g. equivalent per litre.

| Solvent and temp. | Promoter | Conc. of acid or salt soln. × 5 × $10^4$. | Vol. of drop in c.c. × 20. | Critical areas in sq. cm<br>1st Break | Critical areas in sq. cm<br>2nd Break | No. of mol. necessary to produce 1 $cm^2$ of 1st critical area. | $p \times 10^{-14}$. |
|---|---|---|---|---|---|---|---|
| Water at 21° | HCl | *N* | 2·50 | 15·21 | 27·52 | 0·99 | 1·00 |
| | | | 4·23 | 24·88 | 49·43 | 1·02 | |
| | | *N*/2 | 8·74 | 26·48 | 52·74 | 0·99 | |
| | | | 6·20 | 18·60 | 38·42 | 1·00 | |
| Water at 21·1° | $H_2SO_4$ | *N* | 5·31 | 35·80 | 65·12 | 0·44 | 0·88 |
| | | | 3·20 | 21·55 | 45·43 | 0·45 | |
| | | *N*/2 | 6·41 | 22·37 | 40·18 | 0·43 | |
| | | | 7·23 | 24·10 | 44·52 | 0 45 | |
| Water at 21·0° | $H_3PO_4$ | *N* | 4·42 | 30·48 | 53·41 | 0 29 | 0·90 |
| | | | 3·72 | 24·80 | 47·52 | 0·30 | |
| | | *N*/2 | 5·20 | 17·33 | 30·14 | 0·30 | |
| | | | 6·33 | 21·42 | 40·01 | 0·29 | |
| Water at 21·2° | $HNO_3$ | *N* | 4·21 | 23·61 | 40·41 | 1·07 | 1·06 |
| | | | 3·74 | 22·44 | 43·20 | 1·00 | |
| | | *N*/3 | 8·42 | 15·31 | 20·14 | 1·10 | |
| | | | 6·72 | 12·23 | 20·32 | 1·09 | |
| Water at 21·1° | NaCl | 2*N* | 2·60 | 14·18 | 24·10 | 2·22 | 2·23 |
| | | | 4·40 | 24·00 | 42·34 | 2·20 | |
| | | *N*/2 | 9·43 | 12·57 | 28·12 | 2·25 | |
| | | | 8·62 | 11·49 | 24·34 | 2·25 | |
| Water at 21·0° | KCl | 2*N* | 4·42 | 17·68 | 36·12 | 3·00 | 3·01 |
| | | | 5·21 | 20·71 | 38·43 | 3·02 | |
| | | *N* | 8·21 | 16·31 | 29·42 | 3·02 | |
| | | | 6·42 | 12·84 | 24·34 | 3·00 | |
| Water at 21·0° | RbCl | 3*N* | 3·35 | 18·33 | 34·21 | 3·29 | 3·31 |
| | | | 4·42 | 23·96 | 40·43 | 3 32 | |
| | | *N* | 6·52 | 11·85 | 23·14 | 3·30 | |
| | | | 5·47 | 9·86 | 21·23 | 3·33 | |
| Water at 22·1° | CsCl | 4*N* | 4·42 | 29·63 | 60·23 | 3·58 | 3·62 |
| | | | 5·68 | 37·86 | 74·15 | 3·60 | |
| | | *N* | 7·42 | 12·17 | 27·12 | 3·66 | |
| | | | 8·12 | 13·38 | 29·73 | 3·64 | |

TABLE III

| Spreading liquid. | Time of exposure to X-rays in min. | Vol. of drop in c.c. × 20. | Critical area in sq. cm 1st break. | Critical area in sq. cm 2nd break. | Pseudo-acidic normality × 5 × $10^4$. |
|---|---|---|---|---|---|
| Water containing $10^{-7}$ g. of colloidal graphite per g. of water and irradiated by X-ray, Temp. = 22°, | 2 | 7·62 | 20·44 | 43·52 | 0·447 *N* |
| | 4 | 6·82 | 18·82 | 41·42 | 0·460 |
| | 6 | 6·41 | 18·27 | 41·21 | 0·475 |
| | 8 | 6·22 | 18·29 | 40·94 | 0·490 |
| | 10 | 5·84 | 17·66 | 39·12 | 0·504 |
| | 12 | 5·44 | 16·84 | 38·54 | 0·516 |
| | 14 | 5·00 | 15·78 | 37·11 | 0·526 |
| | 16 | 4·62 | 14·80 | 36·44 | 0·534 |
| | 18 | 4·27 | 13·83 | 32·12 | 0·540 |

TABLE IV

| Temperature etc. | $\gamma B =$ Surface tension of Hg. | $\gamma AB =$ Interfacial tension between Hg and solution | $\gamma A =$ Surface tension of water. | Solution. | $\gamma B - \gamma A - \gamma AB$ Harkin's coefficient. | Direct determination of spreading pressure by Torsion balance. |
|---|---|---|---|---|---|---|
| 30°, Unit of γ-dynes/cm | 490 | 420 | 72 | Water | −2 | −10 |
| | 490 | 425 | 72 | HCl soln. | −7 | −15 |
| | 490 | 435 | 72 | $HNO_3$ | −17 | −25 |
| | 490 | 440 | 72 | $H_2SO_4$ | −22 | −27 |
| | 490 | 447 | 72 | Water with colloidal graphite | −29 | −30 |

## DISCUSSION

*Spreading-power Coefficient possessed by Different Types of Ions.*—One sq. cm. surface of mercury contains $10^{15}$ atoms of Hg. For the first critical area to be 1 sq. cm. it is found by calculation that $10^{14}$ molecules of HCl, $0{\cdot}44 \times 10^{14}$ molecules of $H_2SO_4$, $0{\cdot}30 \times 10^{14}$ molecules of $H_3PO_4$ are necessary, showing that about $10^{14}$ $H^+$ ions are necessary to produce 1 sq. cm. of critical area. But from the divergence in the values of $p$ for the four acids, it is clear that the negative ions also play some part in the spreading phenomenon. For the alkali halides the corresponding values are $2{\cdot}2 \times 10^{14}$, $3{\cdot}0 \times 10^{14}$, $3{\cdot}3 \times 10^{14}$ and $3{\cdot}6 \times 10^{14}$ molecules for NaCl, KCl, RbCl and CsCl respectively. Thus the field of force of one adsorbed $H^+$ ion can affect the field of force of 10 atoms in such a way that non-spreading liquids spread easily over Hg. For the alkali halides it can be seen that as the size of the cation becomes bigger, more of such ions must be adsorbed in order to produce the same change in the interfacial tension or interfacial energy.

*The Effect of X-ray Irradiation on Water contaminated with Colloidal Impurities.*—It has been observed by the author that X-ray irradiation of water containing a small amount of colloidal graphite produces varying amounts of spreading power in the solution depending upon the time of illumination. This means that $H^+$ ions with a fair degree of stability have been produced in the liquid, whose number increases with the duration of illumination by X-ray. From the study of the velocity of spreading of these samples of colloidal solutions, it can be inferred that as far as spreading is concerned the charged colloids act in the same way as the ions in acids; and X-rays modify the spreading power. It appears that the structure of the $(H_2O)_n$ aggregates in presence of colloids become less complicated on illumination with X-rays The effect of such irradiation lasts up to 1 hour, and its effect is primarily to produce some $H^+$ ions. With longer period of irradiation the $H^+$ ions so produced, are more efficient in changing the interfacial tension between Hg and irradiated solution. This fact, as well as the study of the depolarisation of light scattered by these solutions reveal that the ions produced are clusters of the type $H^+-(H_2O)_n$ and longer irradiation decreases the value of $n$, *i.e.*, the clusters grow smaller with longer period of irradiation. The spreading of conductivity water containing traces of fluorescent dyestuff, on Hg surface will be treated in a future paper. In Table III, the pseudo-acidic normality of such water has been calculated by assuming that

$10^{14}$ ions are necessary to produce 1 sq. cm. of critical area and that the pseudo-acid so produced is monovalent.

*Spreading Pressure and Adsorption.*—The nature of pressure, producing spreading in the initial stage (before the first break) may be of the same type as is present in the adsorption of multimolecular layer of undissociated vapour. or dissociated ion on solid surfaces. Here the field of the spreading force exerted by Hg atoms is very feeble and the spreading pressure is entirely due to higher ionic layers adsorbed temporarily ever the first weakly adsorbed layer. But from the first break onward the field of force exerted by Hg atoms comes into operation, of course modified by the field of force of higher adsorbed layers. From the second break onward the spreading is almost entirely controlled by the field of the Hg atoms. Rowley and Innes (*J. Phys. Chem.*, 1942, **46**, 694) have discussed the nature of these spreading pressures in the case of multi-molecular and multi-ionic adsorbed layers.

*Interfacial Tension between* Hg *and solution and Direct Measurement of Spreading Pressure.*—From an inspection of Table IV, it is clear that even with negative Harkin's coefficient spreading is possible. This is also verified by direct torsion balance measurement. This shows that other forces besides those present in Harkin's coefficient must be operative in the spreading phenomena. There may be extra superimposition of Van der Waal, electrostatic, or exchange forces.

*Spreading of Conductivity Water on* Hg.—The equation according to which conductivity water spreads on Hg surface fits in well with the formula

$$D=0\cdot0824t^{\frac{3}{4}} \quad \text{for volume } 0\cdot504 \text{ c.c. or with } v=0\cdot0309/t^{\frac{1}{4}}$$

where $v$ is the velocity of spreading, $D$ is the diameter of the drop and $t$, the time of spreading. Similar equation has been developed by Blasius (*Z. Math. Phys.*, 1908, **1**, 56) for the motion of a rectangular foil of length $l$, breadth $b$, over the surface of water possessing interfacial tension $\gamma$ between the foil and the film of water, density $\rho$, and coefficient viscosity $\eta$.

$$\gamma=\frac{1\cdot327}{\cdot2}\sqrt{\eta\rho l u^3} \qquad \text{or} \qquad u=\left[\frac{4\gamma^2}{(1\cdot327)^2\eta\rho l}\right]^{\frac{1}{3}}.$$

From dimensional considerations in the case of the spreading of circular film of water of radius $r$ over Hg, $l$ of Blasius's equation has been replaced by $r$, and the nature of the constant in the equation has been generalised by the present author.

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# CHEMICAL ACTIVITY OF HALOGEN DERIVATIVES OF SUBSTITUTED AMIDES OF MALONIC ACID. PART II. VELOCITY OF REPLACEMENT OF CHLORINE ATOM OF THE GROUP -CHCl- IN MONOCHLORO DERIVATIVES OF SUBSTITUTED AMIDES OF MALONIC ACID

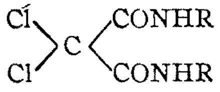
By K. G. Naik, R. K. Trivedi and S. M. Mehta

The following substances have been studied for their chemical activity as expressed by the velocity of replacement of the chlorine atom in them (1) Monochlormalondiphenylamide. (2) Monochlormalondi-*p*-tolylamide. (3) Monochlormalondi-*o*-tolylamide. (4) Monochlormalondi-1:3:4-xylylamide.

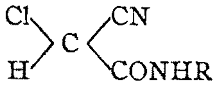
The results indicate that the following factors influence the velocity of replacement of the chlorine atom by hydrogen :

(*i*) The positions of the radicals like the methyl groups in the nuclear rings attached to the carbonyl groups, (*ii*) The molecular weights of the residues carried by the carbonyl groups, (*iii*) The nature of the nuclei attached to the carbonyl groups between which the carbon atom carrying the chlorine atom is situated.

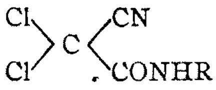
Investigations have been carried out in this laboratory with regard to the stability of chlorine atoms in substances of the following types :—



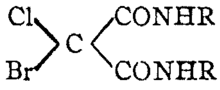
$$\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CONHR}\\\mathrm{CONHR}\end{matrix}$$



$$\begin{matrix}\mathrm{Cl}\\\mathrm{H}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CN}\\\mathrm{CONHR}\end{matrix}$$



$$\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CN}\\\mathrm{CONHR}\end{matrix}$$

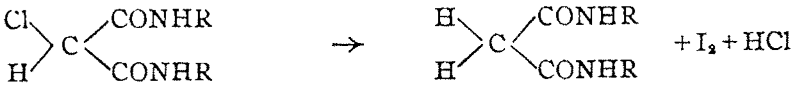


$$\begin{matrix}\mathrm{Cl}\\\mathrm{Br}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CONHR}\\\mathrm{CONHR}\end{matrix}$$

In this paper, are embodied the observations made with regard to the velocity of the replacement of the chlorine atom in the following substances :—(*i*) Monochlormalondiphenylamide. (*ii*) Monochlormalondi-*p*-tolylamide. (*iii*) Monochlormalondi-*o*-tolylamide. (*iv*) Monochlormalondi-1:3:4-xylylamide.

The above substances have been prepared as already described in Part I (*vide this Issue*, p. 345) and experiments have been done to study (*i*) how far the velocity of reduction of the chlorine atom is influenced by the nature of the groups attached to the carbonyl group in the molecule, and (*ii*) whether the symmetry established in the molecule in the case of a compound such as dichloromalondi-1:3:4-xylylamide has a tendency to bring about stability of the chlorine atoms.

The chlorine has been replaced by hydrogen by treating the chloro derivatives with hydriodic acid.



$$\begin{matrix}\mathrm{Cl}\\\mathrm{H}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CONHR}\\\mathrm{CONHR}\end{matrix} \rightarrow \begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CONHR}\\\mathrm{CONHR}\end{matrix} + \mathrm{I_2} + \mathrm{HCl}$$

0·001 Gram mol. of the substance was dissolved in 98% alcohol and the volume was made up to 1 litre. 1 C.c. of this solution was run down from a burette in a conical flask containing a mixture of 2·5 c.c. of *N*/100-potassium iodide solution and 2·5 c.c. of *N*/200-hydrochloric acid solution. Eight such flasks were placed simultaneously at a known time in an electrically regulated thermostat maintained at 30°. At suitable intervals each flask was removed from the thermostat and cooled by adding a piece of ice to the reacting mixture in order to arrest the reaction. The iodine liberated during the reaction was then titrated immediately by means of 0·0004 *N*-sodium thiosulphate solution.

Simultaneously with the above set of experiments an equal number of flasks containing only potassium iodide and hydrochloric acid solution were placed in a thermostat for blank check.

Following is the summary of the results obtained, on studying the velocity of reduction of the chlorine atoms.

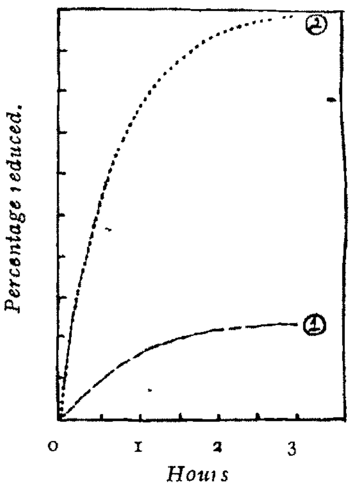
| | Time in hours | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0-15 | 0-30 | 0-45 | 1-00 | 1-30 | 2-00 | 2-30 | 3-00 |
| Name of the substance | Percentage of chlorine replaced | | | | | | | |
| Monochloromalondiphenylamide | 9·60 | 18·40 | 23·00 | 25·50 | 28·80 | 30·00 | 30·60 | 30·90 |
| Monochloromalondi-*p*-tolylamide | 2·60 | 5·30 | 8·40 | 9·70 | 11·40 | 12·80 | 13·60 | 14·00 |
| Monochloromalondi-*o*-tolylamide | 31·00 | 30·80 | 39·60 | 46·00 | 52·80 | 56·80 | 58·00 | 59·20 |
| Monochloromalondi-1.3.4-xylylamide | 14·20 | 26·80 | 35·60 | 41·70 | 48·20 | 52·20 | 54·80 | 55·80 |

In Fig. 1 are drawn the curves for the velocity of the reduction of chlorine in the compounds (*i*) monochloromalondiphenylamide and (*ii*) monochloromalondi-1 : 3 : 4-xylylamide. As between these two, the higher percentage of reduction in the case of the xylyl derivative seems to be the outcome of the high molecular weight of the ring system attached to the carbonyl groups.

The *ortho*-compound shows the highest rate of reduction though the molecular weight of the ring systems in the case of the xylidide derivative is higher; and as such, the latter ought to show the higher rate of reduction than the *ortho*-derivative, as would follow from the above reasoning. The presence of the two methyl groups in the nucleus of the xylidide compound, may mutually influence one another.

From the above considerations, it appears that the following factors govern the velocity of replacement of the chlorine atoms :

FIG. 1

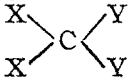


(*i*) The positions of the radicals like the methyl groups in the nuclear rings attached to the carbonyl groups.

(*ii*) The molecular weight of the residues carried by the carbonyl groups.

(*iii*) The nature of the nuclei attached to the carbonyl groups between which the carbon atom carrying the chlorine, is situated.

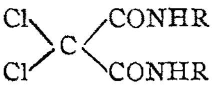
In this connection, reference might be made to the work of Spiers and Thorpe (*J. Chem. Soc.*, 1925, 538), who have shown that the valency pulls in a system like :—



$\begin{smallmatrix}X\\X\end{smallmatrix}>C<\begin{smallmatrix}Y\\Y\end{smallmatrix}$

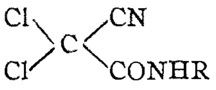
will depend not only upon the nature of the radicals but also upon the symmetry established by these in the whole molecule.

For example, in the following systems :



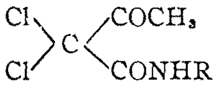
$\begin{smallmatrix}Cl\\Cl\end{smallmatrix}>C<\begin{smallmatrix}CONHR\\CONHR\end{smallmatrix}$

(I)



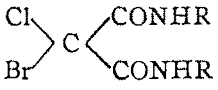
$\begin{smallmatrix}Cl\\Cl\end{smallmatrix}>C<\begin{smallmatrix}CN\\CONHR\end{smallmatrix}$

(II)



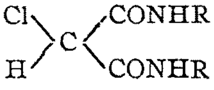
$\begin{smallmatrix}Cl\\Cl\end{smallmatrix}>C<\begin{smallmatrix}COCH_3\\CONHR\end{smallmatrix}$

(III)



$\begin{smallmatrix}Cl\\Br\end{smallmatrix}>C<\begin{smallmatrix}CONHR\\CONHR\end{smallmatrix}$

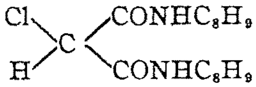
(IV)



$\begin{smallmatrix}Cl\\H\end{smallmatrix}>C<\begin{smallmatrix}CONHR\\CONHR\end{smallmatrix}$

(V)

(II), (III), (IV), (V) are unsymmetrical as compared with (I). The tendency, therefore, in the former, will be such that the chlorine atoms in them will be unstable and could be easily replaced. This is actually observed during the investigations carried out in these laboratories. As for example, in the case of (I), where there is a full symmetry around the central carbon atom, it seems that there is a counterbalancing of pulls, and both the chlorine atoms appear to be attached firmly to the central carbon atom, as no chlorine has been found to be reduced under the experimental conditions. This may help us to surmise why the chlorine atom in the unsymmetrical compound *viz.* :—



is reduced, whereas, the corresponding dichloro derivative remains unaffected.

The authors are grateful to H. H. The Maharaja Gaekwad's Government for necessary facilities given for carrying out the above work.

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# GRAY AND CRUICKSHANK'S METHOD AND THE DIAMAGNETIC SUSCEPTIBILITIES OF DICYANDIAMIDE, ACETAMIDE AND CYANURIC ACID

By Sushil Kumar Siddhanta and Priyadaranjan Rây

Magnetic susceptibilities of dicyandiamide, acetamide, and cyanuric acid have been measured on very carefully purified specimens. The values found have been compared with those calculated by Gray and Cruickshank's method, using the resonating structures established by X-ray analysis of their crystals. A survey of the results indicates that though the values given by Gray and Cruickshank's method of calculation prove to be a decided improvement upon those derived from Pascal's procedure, still the agreement between the experimental and calculated values is not sufficiently close in all cases. In the case of cyanuric acid there is a large difference between the two values for every possible single or resonating structure of the molecule.

Pascal's pioneer work, based on magnetic measurement, has made a notable contribution towards the analysis of molecular structure of organic compounds, except in certain cases of substances containing both nitrogen and oxygen. Gray and Cruickshank (*Trans. Faraday Soc.*, 1935, **31**, 1491) have developed a new method for the magnetic analysis of both resonating and non-resonating molecular structures. Their method of calculation is based on the following factors :—

(*a*) Ionic diamagnetisms, calculated on the basis of a modification of Pauling's formula (*Proc. Roy. Soc.*, 1927, **114A**, 181).

(*b*) Residual charges, due to unequal sharing of bond electrons, calculated from the dipole moments of the bonds.

(*c*) Bond depression of diamagnetism, which, according to these authors, is partly, to a small extent, real lowering of pure diamagnetism, but mainly masking (without lowering) of pure diamagnetism by the development of high frequency paramagnetism, as indicated by quantum mechanical calculations for the simple molecule of hydrogen.

(*d*) Resonance between possible structures for the molecule, each resonating form contributing its due share to the diamagnetism of the resultant molecule.

(*e*) Formation of H-bond where hydrogen-bridges are possible.

A detailed discussion of this method of calculation will be found in their paper (*loc. cit.*).

The present work was undertaken with a view to testing the validity of this method in the case of some simple organic molecules containing nitrogen, for which the Pascal's method usually fails. The compounds selected are dicyandiamide, acetamide and cyanuric acid, the details of whose structures are definitely known from X-ray measurements. The susceptibilities of these compounds, calculated on the basis of Gray and Cruickshank's method, were compared with those experimentally observed. The results, however, did not furnish a consistent and satisfactory agreement. The various values required for calculating susceptibilities were taken from Gray and Cruickshank's paper.

## EXPERIMENTAL

### *Preparation of the Compounds*

*Dicyandiamide.*—Extra pure dicyandiamide (Merck) was recrystallised five times from water and the susceptibilities of the fourth and the fifth fractions were measured.

*Acetamide.*—Merck's extra pure acetamide was distilled twice in vacuum and the purest middle fractions of the first and the second distillate were used. (B.P. 99° at 7 mm. pressure).

*Cyanuric Acid.*—This was prepared by heating urea with anhydrous $ZnCl_2$ at 190-200° in an oil-bath until all ammonia was expelled. The product was washed from all soluble matters with hot water and repeatedly crystallised from conc. HCl (Fe-free). This was finally dried over KOH. The third and fourth fractions were used for susceptibility measurements. {Found (3rd crop) : N, 32·58. $C_3H_3N_3O_3$ requires N, 32·56 per cent}.

### *Measurements*

The susceptibilities were measured according to Guoy's method. The field strength employed was $10·4 \times 10^3$ gauss with a current of 5 amperes. This was determined from a measurement on air-free conductivity water in the same tube in which other measurements were carried out ; the value was corrected for air. The close agreement between values for two consecutive fractions of crystallisation or distillation product was taken as the criterion of purity of the substances concerned. All the measured values were corrected for air. The details of the magnetic balance and the method of measurement have been described in a previous paper from this laboratory (Rây and Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 323).

The results of measurement are expected to be correct within 2 per cent.

The mass susceptibilities were calculated according to the formula :—

$$\chi_g = \frac{2 \times l \times m'}{m \times H^2 \times 1·019} + \chi_v^t / d_s$$

where $\chi_g$ is the gram susceptibility of the substance, $\chi_v^t$ is the volume susceptibility of air at $t°$, the temperature of measurement, $l$= the length of the tube in cm., $m'$= the change of weight in mg., $m$=the weight of the substance in g., $H$=the maximum field strength, and $d_s$ = the density of the substance.

All suceptibility values given below are to be multiplied by $10^{-6}$. The results of measurement are recorded in Table I.

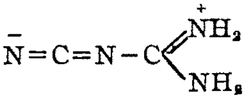
TABLE I

| Substance. | $m$. | $l$. | $m'$. | $\chi_g$ uncorrected. | $d_s$. | $t°$. | $\chi_v^t$. | $\chi_g$ corrected. | $\chi_M$. |
|---|---|---|---|---|---|---|---|---|---|
| 1. Dicyandiamide. | | | | | | | | | |
| (*a*) 4th frac. | 3·404 g. | 11·4 cm. | —9·05 mg. | —0·5501 | 1·404 | 29° | 0·0276 | —0·5304 | —44·55 |
| (*b*) 5th frac. | 3·438 | ,, | —9·14 | —0·5500 | ,, | ,, | ,, | ,, | ,, |
| 2. Acetamide. | | | | | | | | | |
| (*a*) 1st dist. | 4·446 | 11·4 | —11·94 | —0·5558 | 1·159 | 30° | 0·0275 | —0·5321 | —31·39 |
| (*b*) 2nd dist. | 4·356 | ,, | —11·74 | —0·5577 | ,, | ,, | ,, | —0·5340 | —31·52 |
| 3. Cyanuric acid. | | | | | | | | | |
| (*a*) 3rd fract. | 3·173 | 11·4 | — 7·54 | —0·4917 | 1·72 | 31° | 0·0273 | —0·4758 | —61·39 |
| (*b*) 4th fract. | 3·174 | ,, | — 7·58 | —0·4939 | ,, | ,, | ,, | —0·4780 | —61·67 |

The density of cyanuric acid was determined at 30° with xylene as the filling liquid. Densities of other substances were taken from standard tables.

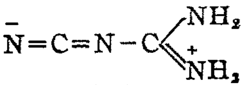
## CALCULATED RESULTS

*Dicyandiamide.*—It has been shown by X-ray analysis that the substance resonates between the structures IA, IB and II. IA and IB contribute 75% in equal amounts and II contributes 25% to the normal state of the molecule (Hughes, *J. Amer. Chem. Soc.*, 1940, **62**, 1258).



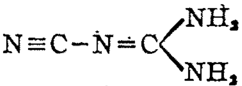
$\overset{-}{N}=C=N-C\left\langle\begin{array}{l}\overset{+}{N}H_2\\ NH_2\end{array}\right.$

(IA)



$\overset{-}{N}=C=N-C\left\langle\begin{array}{l}NH_2\\ \overset{+}{N}H_2\end{array}\right.$

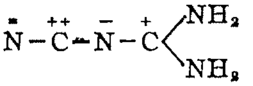
(IB)



$N\equiv C-\dot{N}=C\left\langle\begin{array}{l}NH_2\\ NH_2\end{array}\right.$

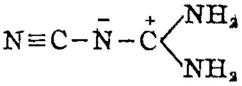
(II)

According to Gray and Cruickshank's method of calculation we may consider IA and IB to be identical as their molecular susceptibilities will be equal. If again each double bond is split up into a polarised single co-valent bond, as suggested by Gray and Cruickshank, then I and II will assume in addition the equivalent structures III and IV respectively.



$\overset{=}{N}-\overset{++}{C}-\overset{-}{N}-\overset{+}{C}\left\langle\begin{array}{l}NH_2\\ NH_2\end{array}\right.$

(III)



$N\equiv C-\overset{-}{N}-\overset{+}{C}\left\langle\begin{array}{l}NH_2\\ NH_2\end{array}\right.$

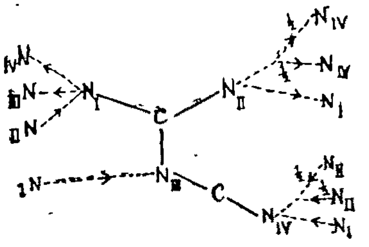
(IV)

Under these circumstances the resultant molecular susceptibility of the compound would be 3/8 due to I, 3/8 due to III, 1/8 due to II and 1/8 due to IV. Let us denote this as case A.

If, however, the triple bond is also supposed to split up like the double bond, then the structure II will likewise lead to an alternative configuration identical with III. The resultant molecular susceptibility under this condition will be made up of 3/8 due to I, 1/8 due to II and the rest 1/2 due to III (case A′).

If, however, we ignore III and IV, the resultant molecular susceptibility will be 3/4 due to I and 1/4 due to II (case B).

Till now we have not considered the H-bonds which play a very important part in building up the crystal lattice. The disposition of H-bonds as found from X-ray analysis is denoted by V.



(V)

The direction of the arrows indicates the N-atoms which accept the H-atoms forming the H-bonds. There is a bifurcated H-bond between $N_{II}$ atom of each molecule and two adjacent $N_{IV}$ atoms of two different molecules.

On consideration of the effect of these H-bonds Gray and Cruickshank's method of calculation gives a new value for the resultant molecular susceptibility for each of the structures I, II, III and IV, and consequently in each of the cases A, A′ and B discussed above. Table II summarises the results of calculation.

TABLE II

Experimental value = 44·55

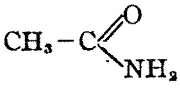
| Structure. | $\chi_M$ (G & C, without H-bonds). | $\chi_M$ (G & C, with H-bonds). | $\chi_M$ Pascal. | Resonance contribution. |
|---|---|---|---|---|
| I | 31·65 | 25·39 | 22·4 | |
| II | 38·41 | 40·73* | 37·0 | |
| III | 58·45 | 59·41 | | |
| IV | 45·66 | 45·49* | | |
| Case A | 44·30 | 43·98 | | 3/8(I)+3/8(III)+1/8(II)+1/8(IV) |
| ,, A′ | 45·90 | 44·32 | | 3/8(I)+1/8(II)+1/2(III) |
| ,, B | 31·84 | 29·23 | 26·1 | 3/4(I)+1/4(II) |

* In calculating these two values it was necessary to assume the absence of bifurcated H-bonds between $N_{II}$ and $N_{IV}$ atoms, since the $N_{IV}$ atom, having only one lone pair of electrons, can receive only one H-bond from outside. In fact, the X-ray analysis also shows that the interatomic distance between $N_{II}$ and $N_{IV}$ atoms is somewhat larger than the N—N distance with a H-bond between them.

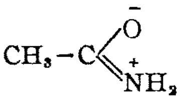
In the above calculations the bond depressions for C—N and N—H bonds have been taken to be equal to those of C—O and O—H-bonds respectively. This is not likely to affect the resultant susceptibility as the values are very small, and particularly since the oxygen and nitrogen atoms are closely similar in respect of weight and electronegativity.

It appears that the resonating structure of case A with or without H-bonds as well as that of A′ with hydrogen bonds give values agreeing closely with experimental results.

2. *Acetamide.*—The acetamide molecule has been found to resonate equally between the structures VI and VII from X-ray analysis of its crystal (Senti and Harker, *J. Amer. Chem. Soc.*, 1940, **62**, 2008).

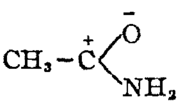


(VI)

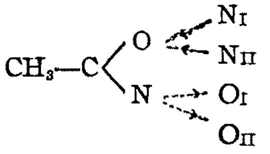


(VII)

The polarised single bond structure VIII will arise in both cases if the double bond is split up as assumed by Gray and Cruickshank.



(VIII)



(IX)

Structure IX shows the distribution of hydrogen bonds in the crystal lattice as found by X-ray analysis. Each H-atom of $NH_2$-group is linked to two oxygen atoms in different adjacent molecules in every structure.

Considering the splitting up of double bonds the resultant molecular susceptibility will be made up of 1/4 due to VI, 1/4 due to VII and 1/2 due to VIII (case A). Otherwise it would arise out of 1/2 the contribution from VI and 1/2 from VII (case B). The values are recorded in Table III.

TABLE III

| Structure. | $\chi_M$ (G & C without H-bonds). | $\chi_M$ (G & C with H-bonds) | $\chi_M$ (Pascal). | Resonance contribution. |
|---|---|---|---|---|
| VI | 30·70 | 33·43 | 26·39 | |
| VII | 28·73 | 30·96 | 24·55 | |
| VIII | 40·14 | 42·36 | | |
| Case A | 34·93 | 37·30 | | 1/4(VI)+<br>1/4(VII)+<br>1/2(VIII). |
| Case B | 29·72 | 32·20 | 25·47 | 1/2(VI) +<br>1/2(VII). |

Experimental value = 31·39, 31·52.

TABLE IV

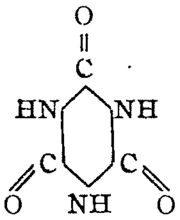
| Structure. | $\chi_M$ (G & C without H-bonds). | $\chi_M$ (G & C with H-bonds). | $\chi_M$ Pascal. | Resonance contribution. |
|---|---|---|---|---|
| X | 39·26 | 43·03 | 35·15 | |
| XI | 38-89 | 37·23 | | |
| XII | 67·73 | 72·04 | | |
| Case A | 51·71 | 55·59 | | 1/6(X)+<br>1/3(XI)+<br>1/2(XII). |
| Case B | 35·69 | 39·14 | | 1/3(X)+<br>2/3(XI). |

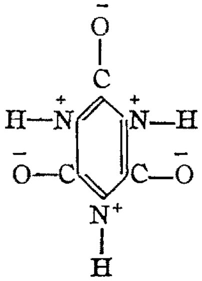
Experimental value = 61·39, 61·67.

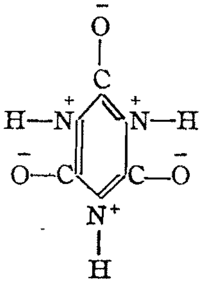
For Gray and Cruickshank's method the nearest approach to the experimental value is found in case B with or without H-bonds, which does not consider the splitting up of double bonds.

3. *Cyanuric Acid.*—The molecule has been found by X-ray analysis to resonate equally among the structures X, XIA and XIB (Wiebenga and Moerman, *Z. Krist.*, 1938, **99**, 217).

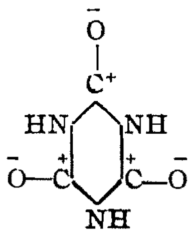
The molar suceptibility, calculated according to Gray and Cruickshank's method will give

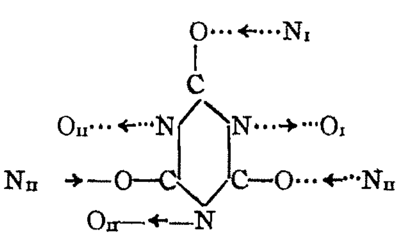

X


XIA


XIB

identical values for XI A and XI B, and each of the structures X, XIA and XIB will assume the configuration XII if the double bonds are split up. Structure XIII shows the distribution of H-bonds in the crystal lattice.


XII


XIII

Considering the splitting up of double bonds the resultant molecular susceptibility, calculated according to Gray and Cruickshank's method, would be 1/6 due to X, 1/3 due to XI (A + B) and 1/2 due to XII (case A). Otherwise it will be made up of 1/3 due to X and 2/3 due to XI (case B). The values are shown in Table IV.

The experimental value does not agree with any of the calculated ones.

## DISCUSSION

A survey of the results obtained in the cases examined shows a decided improvement in the susceptibility values, when calculated according to Gray and Cruickshank's method, over those given by Pascal's procedure. Still, the agreement with experimental values is not in every case close enough to justify its adoption. Besides, where there seems to be a close agreement, *e.g.*, in the case of dicyandiamide (case A, with or without H-bonds, and case A′ with H-bond) as well as in case B of acetamide with hydrogen bond, the anomaly remains that in the former the calculation is based on the splitting of double bonds into polarised single bonds, while in the latter it is ignored. In the case of cyanuric acid, however, the method fails altogether.

Remarkable agreements between experimental values and those calculated on the basis of Gray and Cruickshank's method reported by Clow and co-workers (*Trans. Faraday Soc.*, 1937, **33**, 381, 894; 1940, **36**, 1018) in the cases of urea with its derivatives, organic sulphur compounds and derivatives of $SO_4^=$, $S_2O_3^=$, etc., are open to criticism, as consideration for hydrogen bonds and all types of resonance with their percentage contributions has not been made. In the case of urea, for instance, the two resonating structures, on the basis of Werner's formula, cannot contribute equally to the normal state of the molecule, since the structure resulting from the splitting of double bond must be comparatively much less stable, due to its having a smaller number of co-valent bonds and to the juxtaposition of positive charges.

It might be pointed out in this connection that the splitting of double bond in every case, as susggested by Gray and Cruickshank, has little theoretical justification behind it. The interatomic distance on this view cannot be made to agree with the observed values without some further *ad hoc* assumption.

Unless the method is further refined, it cannot be viewed upon as a reliable means for exploring the structure of molecules.

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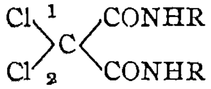
# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART III. THE VELOCITY OF REPLACEMENT OF THE CHLORINE ATOMS IN THE CHLORO DERIVATIVES OF THE SUBSTITUTED AMIDES OF MALONIC ACID

By K. G. Naik, R. K. Trivedi and C. M. Mehta

This study was undertaken to correlate the chemical activity of some chloro derivatives of the substituted amides of malonic acid as expressed by the velocity of replacement of their chlorine atoms with their absorption in the ultraviolet, and to investigate the factors that govern the velocity of replacement of chlorine. It has been found that (1) the curves for the velocity are in general agreement with those of absorption in the ultraviolet, (2) the velocity is augmented by the presence of methyl group in benzene nucleus, (3) the chlorine atoms of the dichloro derivatives are replaced in succession, and (4) the aliphatic straight chain attached to the carbonyl groups increases the rate of replacement.

A study of the chemical activity of the substances mentioned in Table I, was undertaken to correlate this phase of chemical activity of the molecules with their absorption in the ultraviolet. These investigations were undertaken in order to examine how far the velocity of replacement of the chlorine atoms is related to the nature and position of the groups attached to the carbonyl radicles, between which the -$CCl_2$-complex is situated.

If it may be suggested that all the four valencies of the carbon atom are not equal in their intensity with regard to the holding on of the groups attached to them, in a molecule of the type :—



$$\begin{matrix} Cl \diagdown^{1} & & \diagup CONHR \\ & C & \\ Cl \diagup_{2} & & \diagdown CONHR \end{matrix}$$

the tenacity with which the chlorine atoms are held by valency (1) and (2) may not be equal, in which case it is possible that when the chlorine atom attached by valency (1) is removed, the velocity of the removal of the second chlorine atom held by (2) may be much lowered down. This could be attributed either (*a*) to the difference in intensity with which the carbon holds the two chlorine atoms, or (*b*) to the fact that when one of the chlorine atoms is removed, the conditions of the original molecule may undergo such a change that the chemical activity of the molecule as measured by the velocity of the replacement of the second chlorine may be profoundly altered. For this purpose a study of the velocity of replacement of chlorine atoms by hydrogen atoms was undertaken. The chloro compounds were reduced by hydriodic acid (Kurt Meyer, *J. Chem. Soc.*, 1921, **119**, 951, 305). The reaction is represented as

$$Cl_2C(CONHR)_2 + 4HI \longrightarrow H_2C(CONHR)_2 + 2HCl + 2I_2.$$

25 C.c. of the solution of the dichloro compound containing 0·01 g. mol. per litre were mixed in a flask with 10 c.c. of 7·5% potassium iodide solution to which 5 c.c. of hydrochloric acid (*d* 1·16) were added. A battery of 10 such flasks was simultaneously heated under reflux in a water-bath maintained at 100°. At the end of each interval of fifteen minutes, one of the flasks was removed from the bath and cooled by immersing in ice-cold water to arrest the reaction. The iodine liberated was then immediately titrated by 0·0477 *N*-sodium thiosulphate solution.

Fig. 1 represents the curves for the velocity of replacement of chlorine in (1) dichloromalon-diphenylamide, (2) dichloromalon-di-*p*-tolylamide, (3) dichloromalon-di-*m*-chlorotolylamide, (4) dichloromalon-di-*o*-tolylamide, (5) dichloromalon-di-1 : 3 : 4-xylidide, (6) dichloromalon-di-*p*-chloronaphthylamide.

TABLE I

D = Dichloromalon. C = Chloromethylchloromalon.

| Names of compounds. | h.m.<br>0-15 | h.m.<br>0-30 | h.m.<br>0-45 | h.m.<br>1-0 | h.m.<br>1-15 | h.m.<br>1-30 | h.m.<br>1-45 | h.m.<br>2·0 | h.m.<br>2-15 | h.m.<br>2-30 | h.m.<br>2-45 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| D-diphenylamide | 10·17 | 19·56 | 27·67 | 34·11 | 40·30 | 44·84 | 48·42 | 51·75 | 54·85 | 57·24 | 59 86 |
| D-di-*p*-tolylamide | 11·45 | 20·03 | 28·14 | 34·58 | 41·02 | 45·79 | 49·13 | 52·23 | 55·10 | 57·95 | 61·05 |
| D-*m*-chlorotolylamide | 9·63 | 18·84 | 27·67 | 34·10 | 40·30 | 45·17 | 50·08 | 53·18 | 56·04 | 58·91 | .... |
| D-di-*o*-tolylamide | 14·40 | 27·66 | 39·59 | 48·89 | 53·45 | 58·20 | 62 96 | 67·02 | 69·88 | 71·55 | 73·46 |
| D-di-1 : 3 : 4-xylidide | 14·79 | 28·38 | 40·30 | 51·04 | 57·58 | 63·68 | 67·73 | 71·07 | 73·22 | 74·74 | 76·56 |
| D-di-β-naphthylamide | 5·72 | 10·73 | 15·63 | 20·03 | 23·62 | 27·31 | 30·53 | 33·87 | 37·20 | 40·54 | ... |
| D-diheptylamide | 14·79 | 34·82 | 44·82 | 54·14 | 59·15 | 64·16 | 69·64 | 72·50 | 75·13 | 77 27 | 79·18 |
| D-dipropvlamide | 10·49 | 24·56 | 35·77 | 41·38 | 48·65 | 52·95 | 58·08 | 62·59 | 66·30 | 70·36 | ... |
| D-dibenzylamide | 10·02 | 20·75 | 30 87 | 41·50 | 48·65 | 54·85 | 60·58 | 63 57 | 66·66 | 69 16 | 71·35 |
| D-dichlorophenylamide | 12·88 | 25·04 | 33·87 | 40·54 | 45·31 | 49·30 | 51·99 | 53·90 | 54·85 | 55·57 | 56·04 |
| D-mono-*p*-tolylamide | 11·68 | 21·46 | 30·29 | 37·21 | 42·69 | 46·31 | 46·74 | 48·41 | 49·30 | 50·08 | 51·27 |
| C-diphenylamide | 8·11 | 16·69 | 25·28 | 32·91 | 38·16 | 41·97 | 46·27 | 58·89 | 51·52 | 54·38 | 56·73 |
| C-di-*p*-tolylamide | 6·68 | 12.40 | 17·17 | 20·99 | 24·80 | 29·33 | 31·96 | 34·82 | 36·73 | 37·68 | 38·64 |
| C-di-*o*-tolylamide | 1·43 | 4·77 | 7·63 | 10·02 | 12·40 | 14·07 | 15·74 | 17·17 | 17·68 | 18·13 | 18·60 |

It is seen from a comparison of the curves in Fig. 1 of this part with those in Fig. 1 of part I of this series (*J. Indian Chem. Soc.*, 1938, **25**, 421) that the velocity of replacement of the chlorine atoms and the absorption in the ultraviolet are in general agreement. In the order of the increasing velocity of replacement of chlorine atoms, the substances can be arranged as 1, 4, 3, 2, 5 (*vide* Table I).

FIG. 1

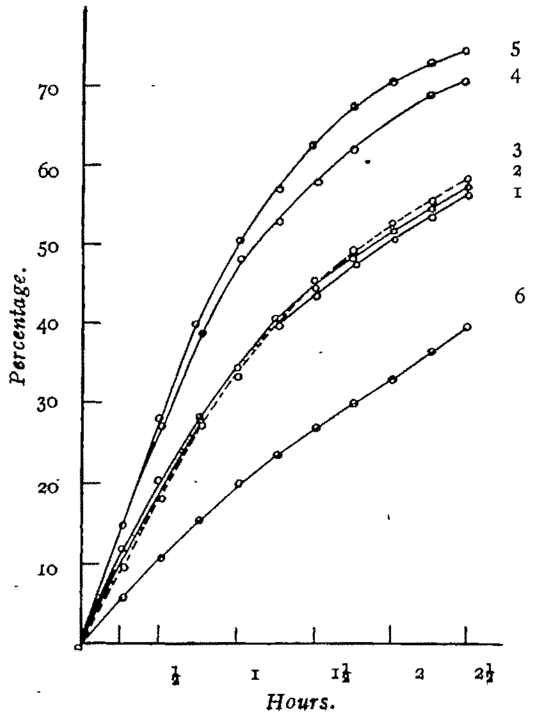
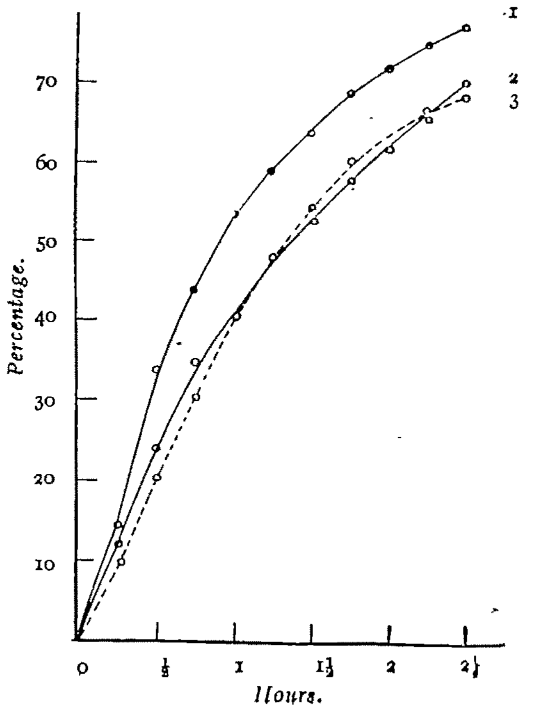


FIG. 2



In this connection a corresponding order is also noticed in the absorption spectra of the same substances. It has also been observed that on the whole the velocity of replacement of chlorine atom by hydrogen atom is augmented by the presence of a methyl group in the benzene nucleus. Further, the position of the methyl group in the nucleus also exerts a considerable influence on the velocity of replacement of the chlorine atoms.

Another point of interest which emerges out is the fact that in each case the velocity of replacement is considerably lowered when 50% of the total chlorine are reduced.

For example, in the case of dichloromalon-diphenylamide, during first fortyfive minutes 27·67% of chlorine are reduced; whereas after two hours (when almost 50% of chlorine are already reduced during next fortyfive minutes) only 8·11% are reduced (59·86—51·75=8·11). This is borne out by the nature of the curve (1) in Fig 1. A closer reference to Table I will reveal that such behaviour is exhibited by all substances.

Further both the chlorine atoms in a compound like -RNHCO·$CCl_2$·CONHR- do not seem to be replaced simultaneously by hydrogen atoms. As a matter of fact the mechanism of the replacement could be represented as

$$Cl_2C(CONHR)_2 + H_2 \longrightarrow CHCl(CONHR)_2 + H_2 \longrightarrow CH_2(CONHR)_2.$$

That the chlorine atoms are not simultaneously removed is borne out by the following considerations:—

(1) If the chlorine atoms were replaced simultaneously there would not have been a big drop in the velocity of replacement after 50% of the total chlorine had been reduced.

(2) That the interaction of these dichloro compounds with phenylhydrazine takes place in two distinct stages, wherein the chlorine atom is removed in succession (*vide* Part IV of this series).

In Fig. 2 are traced the curves (1) dichloromalon-diheptylamide, (2) dichloromalon-dipropylamide, and (3) dichloromalon-dibenzylamide.

These curves explicitly indicate that when the radicals attached to the carbonyl groups carry aliphatic straight chain, the velocity of replacement of chlorine is increased (*vide* curve 1, Fig 2). If the chain is shorter, the velocity is decreased (*vide* curve, 2, Fig 2). It is also decreased when the radical is in the form of a cyclic structure with the same number of carbon atoms (*vide* curve 3 which has the same number of carbon atoms as in curve 1).

FIG. 3

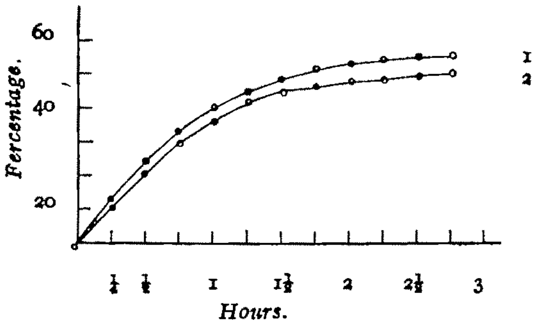
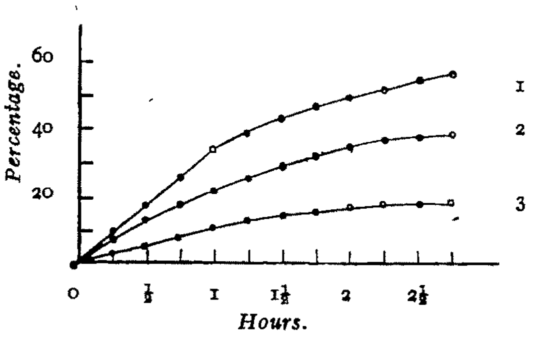


FIG. 4



Here, again, the agreement between the curves expressing the velocity of replacement of the chlorine atoms by hydrogen and the curves expressing the absorption in the ultraviolet is excellent (*cf.* Fig. 3, part I of this series, *loc. cit.*, p. 423).

In Fig. 3 are drawn the curves for the velocity of replacement (1) dichloromalon-mono-chlorophenylamide, and (2) dichloromalon-mono-*p*-tolylamide. These curves show a curious drop in the velocity of replacement of chlorine atoms due to the presence of only one heavy radical in this case, as compared with the corresponding malonamides.

In Fig. 4 are drawn the curves for the velocity of replacement of chlorine atoms in compounds (1) chloromethyl-chloromalon-diphenylamide, (2) chloromethylchloromalon-di-*p*-tolylamide, and (3) chloromethylchloromalon-di-*o*-tolylamide.

The remarkable decrease in the velocity of replacement of chlorine atoms of these chloro derivatives may be attributed to the presence of the $ClH_2C$-grouping.

It may finally be pointed out that there is a close agreement between the curves expressing the velocity of replacement of chlorine atoms (*vide* Figs. 1-4 in this part) and the curves showing the absorption in the ultraviolet in the case of the same substances so far studied (*vide* Figs. 1, 2, 3 and 4, Part I of this series, *loc. cit.*).

The authors are grateful to H. H. the Maharaja Gaekwad's Government for necessary facilities given for carrying out the above work.

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# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART IV. THE INTERACTION OF PHENYLHYDRAZINE WITH THE CHLORO DERIVATIVES OF THE SUBSTITUTED AMIDES OF MALONIC ACID

By K. G. Naik, R. K. Trivedi and C. M. Mehta

The interaction of the chloro derivatives of the substituted amides of malonic acid with phenylhydrazine has been studied under different conditions of temperature and the molecular quantities of the reactants.

The chemical activity of the chloro derivatives as measured by (*a*) the absorption in the ultraviolet (*cf.* part I), and (*b*) the velocity of saponification (*cf.* part II) and (*c*) the velocity of replacement of the chlorine atoms by hydrogen (*cf.* part III), has already been studied. This part is devoted to a study of the interaction of the following chloro derivatives with phenylhydrazine :—

(1) Dichloromalon-diphenylamide. (2) Dichloromalon-di-*p*-tolylamide. (3) Dichloromalon-di-*o*-tolylamide. (4) Dichloromalon-di- 1 : 3 : 4-xylidide. (5) Dichloromalon-di-*m*-chlorotolylamide. (6) Dichloromalon-mono-*p*-tolylamide. (7) Dichloromalon-monochlorophenylamide. (8) Chloromethylchloromalon-di-*p*-tolylamide. (9) Chloromethylchloromalon-di-*o*-tolylamide.

The first member of the series was made to react with phenylhydrazine in boiling alcohol. The reaction mixture was heated under reflux on a water-bath for three hours at the end of which fine crystalline compound separated in the form of yellow bulky silky needles. The reaction is represented thus

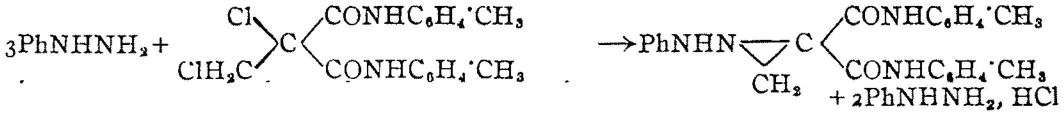
$$3PhNHNH_2 + Cl_2{:}\ C\ (CONHPh)_2 \longrightarrow PhNHN{:}\ C(CONHPh)_2 + 2PhNHNH_2,\ HCl. \qquad \text{(I)}$$

Dichloromalon-di-*m*-chlorotolylamide reacted with phenylhydrazine in a similar way as shown below :

$$3PhNHNH_2 + Cl_2{:}C(CONHC_6H_3Cl{\cdot}CH_3)_2 \longrightarrow PhNHN{:}C(CONHC_6H_3Cl{\cdot}CH_3)_2 + 2PhNHNH_2, HCl \qquad \text{(II)}$$

That the reaction proceeds as above is proved by the fact that on hydrolysis of compound (II), *p*-chlorotoluidine is obtained as one of the products of hydrolysis. This would not have been the case if the chlorine atom situated in the toluidine nucleus had been replaced by phenylhydrazine. Dichloromalon-monochlorophenylamide reacts in the same way as shown above when treated with phenylhydrazine. The most important fact which emerges out from the above reactions is that when phenylhydrazine reacts with compounds having halogens in the nucleus, the nuclear chlorine atoms are not easily removed but that the labile halogens attached to the methylene carbon atoms are removed (Chattaway and Orton, *J. Chem. Soc.*, 1901, **79**, 461).

In the case of chloromethylchloromalon-di-*ortho*- and *para*- tolylamides, phenylhydrazine reacts to give a three membered ring compound thus :—



$$3PhNHNH_2 + \begin{matrix}Cl\\ ClH_2C\end{matrix}\!\!>C<\!\!\begin{matrix}CONHC_6H_4\cdot CH_3\\ CONHC_6H_4\cdot CH_3\end{matrix} \longrightarrow PhNHN\underset{CH_2}{\bigtriangledown}C<\!\!\begin{matrix}CONHC_6H_4\cdot CH_3\\ CONHC_6H_4\cdot CH_3\end{matrix} + 2PhNHNH_2, HCl$$

(III) *para* and *ortho*

The above three-membered ring compound is fairly stable and resists decomposition when boiled with water. This is in accordance with the work of Perkin and Simonson (*J. Chem. Soc.*, 1909, **95**, 1165).

Further it is remarkable that these compounds are formed with great ease and the yield in each case is almost quantitative. The ease with which such three-membered ring compounds are formed and their comparative stability have also been the experience of other workers (Ingold, *J. Chem. Soc*, 1921, **119**, 951, 305; Naik, *ibid.*, 1921, **119**, 376, 1166.)

Again in order to investigate whether the chlorine atoms of the chloro derivatives of the substituted amides of malonic acid interact with phenylhydrazine successively or simultaneously, the following compounds have been selected for study :—

(10) Dichloromalon-diphenylamide. (11) Dichloromalon-di-*p*-tolylamide. (12) Dichloromalon-di-*m*-chlorotolylamide. (13) Dichloromalon-di-*o*-tolylamide. (14) Dichloromalon-di-1 : 3 : 4-xylidide.

The above chloro compounds have been reacted with phenylhydrazine in the cold. The first member of the series is obtained by the interaction of the dichloromalon-diphenylamide with phenylhydrazine. The mixture of the reacting substances is kept in alcohol for eighteen hours (overnight) when a crystalline substance is obtained. The interaction in this case proceeds as follows :—

$$2PhNHNH_2 + Cl_2 : (CONH\cdot Ph)_2 \longrightarrow ClC(CONH\cdot Ph)_2.NH\cdot NHPh + PhNHNH_2, HCl$$

The compounds 11, 12, 13 and 14 react in a similar way. From this it appears that the mechanism of replacement of chlorine atoms is of a graduated nature, one chlorine atom being removed easily and another with difficulty. To remove both the chlorine atoms a drastic reaction is necessary.

## EXPERIMENTAL

### *Interaction of Dichloromalon-diphenylamide with Phenylhydrazine*

(*a*) Dichloromalon-diphenylamide (1 mol. 3·2 g.) was dissolved in alcohol (40 c.c ) and phenylhydrazine (3 mols., 3·3 g.) and the mixture heated under reflux on a water-bath for 3 hours when the compound separated. It was then filtered hot at the pump, washed with alcohol and ether to remove excess of phenylhydrazine and crystallised from benzene in yellow tiny needles. Whereas compound Nos. 2, 3, 4, 5, 6, 7, 8, and 9 were prepared in the same way as No. 1, compound Nos. 10, 11, 12, 13 and 14 (*vide* table annexed) were prepared by the following method.

(*b*) Dichloromalon-diphenylamide (1 mol., 3·2 g.) was dissolved in alcohol (60 c c.) and phenylhydrazine (2 mols., 2·16 g.). The mixture was kept for 24 hours at room temperature when a compound separated in white tiny plates. It was then transferred into a crystallising dish and kept at room temperature for a couple of hours. It was then filtered, washed with alcohol and ether to remove excess of phenylhydrazine. Crystallised from alcohol it separated in tiny white plates. The properties and analyses of all these compounds are given below the annexed table.

| No | Name of the compound. | M.p. | Crystalline structure. | Solubility. | Analysis | |
|---|---|---|---|---|---|---|
| | | | | | Found. | Calc. |
| 1. | Meso-oxalyl-dianilide phenylhydrazone. $C_{21}H_{18}O_2N_4$. | 175° | Yellow tiny needles. | Soluble in benzene, chloroform; less soluble in alcohol, acetic acid and practically insoluble in petroleum. | N, 16·05% | N, 15·65% |
| 2. | Meso-oxalyl-di-*p*-toluidide phenylhydrazone $C_{23}H_{22}O_2N_4$. | 185° | Yellow silky naedles | ,, | N, 14·58 | N, 14·50 |
| 3. | Meso-oxalyl-di-*o*-toluidide phenylhydrazone $C_{23}H_{22}O_2N_4$. | 148° | Yellow shining tiny needles | ,, | C, 71 16<br>H, 5·60<br>N, 14 70 | C, 71 50<br>H, 5·70<br>N, 14·50 |
| 4. | Meso-oxalyl-di-1:3:4-xylidide phenylhydrazone. $C_{25}H_{26}O_2N_4$. | 172° | Yellow crystals | ,, | N, 13 71 | N, 13·50 |
| 5. | Meso-oxalyl-di-*m*-chlorotoluidide phenylhydrazone $C_{23}H_{20}O_2N_4Cl_2$. | 196° | Yellow silky needles | ,, | N, 12·38<br>Cl, 15·43 | N, 12·30<br>Cl, 15·6 |
| 6. | Meso-oxalyl mono-*p*-toluidide phenylhydrazone. $C_{16}H_{16}O_2N_4$. | 195° | Yellow needles | ,, | N, 19 04 | N, 18·92 |
| 7. | Meso-oxalyl monochlorophenylamide phenylhydrazone $C_{15}H_{13}O_2N_4Cl$. | 189-90° | Light yellow needles | ,, | N, 17 73<br>Cl, 11 13 | N, 17·70<br>Cl, 11·22 |
| 8. | 1-Anilo-2: 2-di-*o*-tolylcarbamido-aziridine $C_{24}H_{24}O_2N_4$ | 145° | Greenish yellow needles | ,, | C, 71·83<br>H, 5·95<br>N, 14·20 | C, 72·00<br>H, 6·00<br>N, 14·00 |
| 9. | 1-Anilo-2:2-di-*p*-tolylcarbamido-aziridine $C_{24}H_{24}O_2N_4$ | 190° | Yellow tiny needles | ,, | C, 71 75<br>H, 6·24<br>N, 14·21 | C, 72·00<br>H, 6·00<br>N, 14·00 |
| 10. | Phenylhydrazino-chloromalon-di-anilide $C_{21}H_{19}O_2N_4Cl$. | 179° | Tiny white plates | ,, | Cl, 9·27 | Cl, 9·00 |
| 11. | Phenylhydrazino-chloromalon-di-*p*-toluidide $C_{23}H_{23}O_2N_4Cl$. | 210-11° | Tiny white shining plates | ,, | Cl, 8 44 | Cl, 8·40 |
| 12. | Phenylhydrazino-chloromalon-di-*m*-chlorotoluidide $C_{23}H_{21}O_2N_4Cl_3$. | 218-19° | White shining plates | ,, | N, 11·56<br>Cl, 21·57 | N, 11 39<br>Cl, 21·70 |
| 13. | Phenylhydrazino-chloromalon-di-*o*-toluidide $C_{23}H_{23}O_2N_4Cl$. | 158° | Shining white plates | ,, | Cl, 8·61 | Cl, 8·40 |
| 14. | Phenylhydrazino-chloromalon-di-1:3:4 xylidide $C_{24}H_{25}O_2N_4Cl$. | 206° | White plates | ,, | N, 12 14<br>Cl, 8·14 | N, 12 43<br>Cl, 7·88 |

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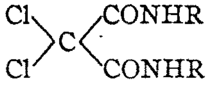
# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART V. THE INTERACTION OF ATOXYL WITH THE HALOGEN DERIVATIVES OF SUBSTITUTED AMIDES OF MALONIC ACID

By K. G. Naik, R. K. Trivedi and C. M. Mehta

Atoxyl is found to be inactive towards chloro derivatives of the substituted amides of malonic acid. It easily reacts with the bromo derivatives.

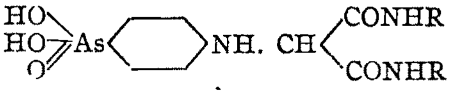
In this part it is proposed to study the reactivity of the chlorine atoms substituted in place of the hydrogens of the reactive methylene group (-$CCl_2$-), with regard to atoxyl. It is known that chloroacetamide and its simpler alkyl derivatives condense readily with atoxyl (Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1919, **41**, 2668). Morgan and Walton (*J. Chem. Soc.*, 1931, 140, 1743) condensed malonyl chloride with *p*-aminophenylarsonic acid.

It has been observed that even under varying experimental conditions atoxyl does not react with the chloro derivatives of the substituted amides of malonic acid of the type (I). This could be attributed to the comparative inactivity or lesser lability of chlorine atoms towards atoxyl.



where R=phenyl, tolyl, etc.

(I)



where R=$C_6H_4Br$ or $C_6H_4 \cdot CH_3$ or $C_6H_5 \cdot CH_2$

(II)

On the other hand the bromine atom substituting the hydrogen of the reactive methylene group (-CHBr-) reacts with atoxyl easily. This could be attributed to the fact that bromine atoms are comparatively labile than similarly situated chlorine atoms. For this purpose the following compounds have been selected.

(1) Monobromomalon-di-*p*-bromoanilide. (2) Monobromomalon-di-*p*-tolylamide. (3) Monobromomalon-dibenzylamide.

It has been found that these compounds react with atoxyl forming compounds of the type (II).

It may be pointed that a study has been made of the compounds of the type, *p*-$H_2O_3As \cdot C_6H_4NH \cdot CH : (CONHR)_2$ by Lewis and Bent (*J. Amer. Chem. Soc.*, 1926, **48**, 949; Kennedy, *J. Chem. Soc.*, 1932, 2781).

The resultant compounds, when treated with ice-cold sodium nitrite and hydrochloric acid and alkaline $\beta$-naphthol, give the characteristic nitroso reaction indicating the presence of the (=NH) imino grouping in the molecule.

## EXPERIMENTAL

*Interaction of Monobromomalon-di-*p*-bromoanilide with Atoxyl.*—2·3 G. of monobromomalon-di-*p*-bromoanilide, m.p. 236° (1 mol.), were dissolved in 50 c.c. of of ethyl alcohol to which 1·7 g. of atoxyl (1 mol.) in 15 c.c. of water were added. It was then heated under reflux in a water-bath for about three hours, when voluminous precipitates separated from the reaction mixture in the form of tiny clusters. The compound was then filtered off from the mother- liquor while cold and crystallised from a mixture of alcohol and acetic acid (50%) (animal charcoal), m. p. 251-53° (decomp.). It is practically insoluble in alcohol, water, acetic acid, benzene, and petroleum ether, and less soluble in a mixture of alcohol-water and alcohol-acetic acid. (Found: As, 11·75; Br, 25·63. $C_{21}H_{18}O_5N_3BrAs$ requires As, 11·96; Br, 25·51 per cent).

The other compounds were prepared in a similar way and are described in Table I.

TABLE I

| Name of compound. | M.p. | Crystalline structure. | Solubility. | Analysis<br>Found. | Calc. |
|---|---|---|---|---|---|
| *p*-Arsono-anilino-malon-di-*p*-tolylamide<br>$C_{23}H_{24}O_5N_3As$. | 233° (decomp.) | Shining tiny crystals. | Insoluble in alcohol, water, acetic acid and less soluble in 50% mixture of alcohol and acetic acid | As, 15·10%<br>N, 8·62 | 15·13%<br>8·45 |
| *p*-Arsono-anilino-malon-dibenzylamide.<br>$C_{23}H_{24}O_5N_3As$. | 266° (decomp.) | Tiny clusters. | Sparingly soluble in alcohol, water, acetic acid and soluble in 50% mixture of alcohol-water and alcohol-acetic acid. | As, 15·24<br>N, 8·36 | 15·13<br>8·45 |

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# FATTY ACID COMPOSITION OF TOBACCO SEED OIL

C. VENKATARAO, M. NARASINGARAO AND A. VENKATESWARULU

The oil from Virginia tobacco seeds of Guntur District (Madras) has been examined and the fatty acid composition determined. Mixed fatty acids consist of myristic (1·8%), palmitic (7·8%), stearic (5·6%), oleic (30·2%) and linoleic (54·6%). The oil contains 1·9% non-saponifiable matter which is mainly sitosterol (m.p. 141°).

Tobacco plant belongs to the natural order *Solanaceae* and to the genus *Nicotiana*, subdivided into the species *Nicotiana rustica* and *Nicotiana tobacum*. The present investigation deals with the seed oil of Virginia tobacco belonging to the species *Nicotiana tobacum*. The total acreage under tobacco cultivation in the Madras Presidency for the year 1941-42 was about 334,000 acres out of which Virginia variety occupied 129,000 acres. Out of this, Guntur district alone contributed 87,000 acres (Madras Agrl. Dept. personal communication), the average yield of seed per acre from the Virginia variety being about 175 lbs. The total production of seed in this district works out to be 6800 tons which on solvent extraction would give about 2000 tons of oil and 4800 tons of seed cake.

The oil from the seeds has been investigated by several workers and its particular property of drying has also been studied. In Guntur district, which stands foremost in tobacco cultivation in South India, the seeds are not utilised for any useful purpose except as cattle fodder, firstly because of the difficulty of extracting the oil and secondly due to lack of proper initiative in the utilisation of the oil. In other countries the oil is recommended for edible purposes and also as a drying oil (Brambilla and Balbi, *Chim. et' Ind.*, 1938, **20**, 548).

In view of the importance of tobacco cultivation in this district, great prominence is attached to the profitable utilisation of the seed which will add to the material benefit of the farmer. With this view the indigenous oil has been subjected to a thorough chemical investigation and the fatty acid composition and glyceride structure determined as a prelude to its ultimate commercial exploitation.

## EXPERIMENTAL

Fresh seeds of Virginia tobacco grown in the district were collected in March 1943 and the oil was extracted with carbon tetrachloride after thoroughly grinding the seed in a buhr-stone. The yield of the oil is 28%. The analytical figures of the oil along with those of the previous workers in other countries are given in Table I.

### *Fatty Acid Composition*

200 G. of the oil were saponified with alcoholic soda and the non-saponifiables removed by extracting the soap with ether after thoroughly mixing it with asbestos. The fatty acids were liberated and subjected to Twitchell's lead salt-alcohol and other method of separation (Twitchell, *Ind. Eng. Chem.*, 1921, **13**, 806). The fatty acid portions obtained from lead-salts soluble in alcohol (A) and in ether (E) were converted into their respective methyl esters and fractionated at 0·2 mm. pressure. The fatty acids from the insoluble lead salts (S) were separated by fractional crystallisation of their barium salts by Heintz method, as the quantity was small for fractionation.

TABLE I

| Constants. | Present workers.* | Greek tobacco seed oil. | Philippine oil (Cruz & West). | Morozov & Graschim. | Beliaev. | Rao & Anjanyuln. |
|---|---|---|---|---|---|---|
| Sp. gr. | 0·9405 at 36·3° | at 20° 0·9440<br>0·9253 | at 30° 9130 | 0·9259 | 0·9254 | 0·9254 at 16° |
| Ref. index | 1·460 at 37° | at 25° 1·4735<br>1·4828 | at 30° 1·4714 | 1·4756 | | |
| Acid. val. | 0·7024 | 2·25 to 16·93 | 16·8 | 2·57 | 9 | |
| Iodine val. | 112·2 | 117·8<br>137·9 | 135·8 | 135·46 | 135·34 | 142 |
| Sap. val. | 191·2 | 186·8 | 190·5 | 194·6 | 200·7 | |
| Non sap.% | 2·0 | — | 1·41 | 1·53 | — | |
| Hehner val. | 93 | 96·21 to 96·3 | — | — | — | |

TABLE II

| | Wt. | Sap. equiv. | I. Val. |
|---|---|---|---|
| Oil | 200 g. | 293·4 | 112·2 |
| Mixed acids | 182 g. | 237·7 | 120·6 |
| EtOH soluble acids (A) | 56 g. | 278·6 | 144·4 |
| Ether soluble acids (E) | 97·5 g. | 267·9 | 126·8 |
| Alcohol soluble acids (S) | 28·5 g. | 277·7 | 54·40 |
| Esters (A) | — | 294·9 | 139·2 |
| Esters (E) | — | 285·6 | 127·6 |

* Due to the freshness of the seed and its immediate extraction with carbon tetrachloride the present sample has a low acid value (0·7% as oleic acid). It is also characterised by a lower iodine value probably due to the climatic conditions.

TABLE III

*Esters (A)*

| Fr. No. | Temp. | Fr. wt. | Sap. eqiv. | I. V. | Identifications. |
|---|---|---|---|---|---|
| 1 | 110-50° | 4·8 g. | 286·1 | 126·1 | M, P, O, L. |
| 2 | 150-55° | 10·2 | 291·3 | 143·7 | P. O., & L. |
| 3 | 156-59° | 9·4 | 294·3 | 150·9 | O & L. |
| 4 | 159-61° | 19·0 | 294·4 | 150 | — — |
| 5 | Residue. | 14·6 | 295 2 (corr.) | 120·9 | — — |

TABLE IV

*Esters (B)*

| Fractions at | Fr. wt. | Sap. eqiv. | I. V. | Identifications |
|---|---|---|---|---|
| 112-45° | 5·4 g. | 278·7 | 121·4 | M, O & L. |
| 145-46° | 24·2 | 292·8 | 142·9 | P O & L. |
| 146-52° | 3·8 | 290·0 | 137·9 | P. O & L. |
| Residue | 9·4 | 291·8 | 103·6 | — — |

M=Myristic; O=Oleic; P=Palmitic; L=Linoleic.

TABLE V

*Acids (S)*

| Fr. no. | Fr. wt. | Sap. eqiv. | I. V. | M.p. | Identifications. |
|---|---|---|---|---|---|
| 1 | 1·42 g. | 276 | 0·96 | 53-54° | Palmitic and stearic |
| 2 | 2·8 | 276·1 | 9·35 | 52-53° | Palmatic, stear.ic & Oleic |
| 3 | 0·8 | 277·6 | 15·5 | 52-53° | — — |
| 4 | 2·4 | 283·0 | 21·1 | 55-56° | — — |
| 5 | 12·4 | 280·5 | 66·6 | 51-52° | — — |

Among the saturated fatty acids myristic (m.p. 52°), palmitic (m.p. 62°) and stearic (m.p. 63°) acids were identified by finding out the mixed melting points with authentic samples. Oleic and linoleic acids were identified by alkaline permanganate oxidation (Lapworth and Mottram, *J. Chem. Soc.*, 1925, 1628) when dihydroxystearic acid (m.p. 131°) and tetrahydroxy stearic acid (m.p. 170-71°) were obtained. Further, on brominating the mixed fatty acids tetrabromostearic acid (m.p. 114°) was obtained and no hexabromide could be detected. The percentage composition of the various acids has been calculated from the above fractions and given below along with the figures reported for Philipine, American and Russian oils.

TABLE IV

| | Guntur sample. | | | | Philipine. | American. | | Russian. |
|---|---|---|---|---|---|---|---|---|
| | LA% | E.A.% | S.A.% | Total | (1) | (2) | (3) | (4) |
| | 30·70 | 53·60 | 15·70 | 100 | | | | |
| Myristic | 0·20 | 1·60 | — | 1·8 | 0·05 | — | — | — |
| Palmitic | 0·90 | 4·20 | 2·70 | 7·8 | 7·25 | 3·3 | 9·8 | 10·5 |
| Stearic | — | — | 5·60 | 5·6 | 3·1 | 5·1 | 5·9 | — |
| Arachidic | — | + | ... | — | 0·4 | — | — | — |
| Oleic | 9·10 | 13·70 | 7·40 | 30·2 | 27·1 | 17·1 | 28·0 | 23·8 |
| Linoleic | 20·50 | 34·1 | — | 54·6 | 62·1 | 74·5 | 56·5 | 65·7 |

The palmitic acid content of the oil, which is the characteristic saturated fatty acid of this group of oils, is 7·8 confirming the observation of Hilditch (' Oils, Fats and Waxes,' p. 11). In this respect it differs from kapok and cottonseed oils. Of all the samples reported in the above table Philipine oil alone contains arachidic acid and no trace of arachidic acid could be detected in the present sample.

### *Non-saponifiable Matter*

The non-saponifiable matter consisted of beautiful shining crystalline needles which melted on crystallisation from methyl alcohol-acetone mixture (3 :1) at 140-141° indicating the presence of sitosterol. Further on benzoylation it gave needles which on crystallisation from benzene-alcohol mixture (1:1) melted at 143°, confirming the presence of the above sterol.

The glyceride structure of the oil by the method of bromination of the neutral oil and separation of the bromoglycerides from various solvents is in progress.

(1) Cruz and West, *Phil. J. Sci.*, 1937, **61**, 161.
(2) *J. Amer. Chem. Soc.*, 1934, **56**, 207.
(3( *J. Biol. Chem.*, 1937, **117**, 21.
(4) U. S. S. R. *State Inst. Tobacco Inv.*, Bul., 1929, 61, 20.

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# PHOTOCHEMICAL STUDIES IN GELS. PART I. THE REDUCTION OF FERRIC CHLORIDE BY MANDELIC ACID IN LIGHT OF DIFFERENT FREQUENCIES IN THORIUM PHOSPHATE GEL AS A SOLVENT MEDIUM

By J. C. Ghosh and S. K. Bhattacharyya

The kinetics of the reduction of ferric chloride by mandelic acid in light of frequencies 366 and 436 $\mu\mu$ in transparent and colourless thorium phosphate gel have been studied. The reaction was found to be zero molecular and the velocity constant was found to increase with increasing concentrations of ferric chloride and in fact $\frac{\Delta x}{\Delta t}\Big/ I_{abs}$ was found to remain constant for a particular wave-length which increase with increased in the magnitude of the quanta absorbed. The velocity constant also increases with increasing concentration of mandelic acid and was directly proportional to the intensity of absorbed radiation. The quantum efficiency was found to be very low. The results were compared with those obtained in thorium phosphate sol before gelation and in aqueous solution. The rate of reaction was found to be the same in both sol and gel states of thorium phosphate but in water it was considerably greater. The extinction coefficients of ferric chloride in presence of excess mandelic acid were measured in all the three media. A mechanism has been suggested.

Photochemical reactions in liquid as well as in gaseous phase have been studied in considerable details but in comparison very few reactions have been studied in gel or solid phase. As examples, we may cite the decomposition of silver halides in gelatine studied by a number of workers, notably by Eggert and Noddack (*Sitzunsgber. preuss. Akad.*, 1923, p. 116; 1921, p. 631; *Z. Physik*, 1925, **31**, 922) in wave-lengths 365, 406 and 436 $\mu\mu$ and the decomposition of AgCl (sensitised by Ag) on printing out paper studied by Weigert (*Sitzungsber. preuss. Akad.*, 1921, p. 641) in wave-length 436 $\mu\mu$. But no worker has, uptil now, made any comparative study of the kinetics of any reaction in both liquid as well as in the gel phase. It would therefore be very interesting if methods could be devised by means of which photochemical reactions could be studied in gel phase and the results compared with those studied in liquid phase. With this idea in mind, we started our work using some transparent and colourless thixotropic gel as solvent medium. The advantage of using thixotropic gels is that they liquefy on shaking which set again on standing for some time.

In the present investigation we have used thixotropic thorium phosphate gel which is transparent, colourless and firm as the medium and have studied a very simple reaction—the photoreduction of ferric chloride by mandelic acid whose kinetics in aqueous solution were studied by various workers, notably by Ghosh and Purkayastha (*J. Indian Chem. Soc.*, 1929, **6**, 827), Benrath (*Z. physikal. Chem.*, 1910, **74**, 115), Winther and Oxolt-Howe (*Z. wiss. Phot.*, 1914, **14**, 196) and by Bolin (*Z. physikal. Chem.*, 1914, **87**, 490).

We have studied the reaction in media of (1) thorium phosphate gel, (2) thorium phosphate sol and (3) water and have made a comparative study of the photoprocess under these conditions.

In aqueous phase, (*i*) the reaction is zero-molecular with respect to ferric chloride. (*ii*) The zero-molecular velocity constant increases with increasing concentration of the reductant and in fact, $\frac{1}{\Delta x/\Delta t}$ plotted against $\frac{1}{[\text{Reductant}]}$ gives a straight line. (*iii*) The velocity constant is directly proportional to the intensity of absorbed radiation. (*iv*) The velocity constant varies very slightly with increasing concentration of hydrochloric acid. (*v*) The quantum efficiency was found to be 1·06, 1·18 and 1·36 in wave-lengths 488, 448 and 390 $\mu\mu$ respectively.

The reaction may be expressed by the equation,

$$2\,FeCl_3 + C_6H_5CH(OH)COOH \longrightarrow 2\,FeCl_2 + 2HCl + CO_2 + C_6H_5CHO.$$

## EXPERIMENTAL

The experimental arrangement was the same as was described by the authors in previous works (*Z. physikal.Chem.*, 1936, **B 32**, 145; *J. Indian Chem. Soc.*, 1941, **18**, 257) with a few alterations *viz.* (*a*) the source of light was a mercury arc lamp whose strength of current and voltage were maintained constant by means of a regulating resistance; (*b*) the reaction cell was 4 cm. × 4 cm. × 1 cm. thick and made of plane glass plates fused into one another with a stopper at the top; (*c*) parallel beams of light were obtained by means of a quartz cylindrical lens.

*Reagents.*—Kahlbaum's extra pure ferric chloride and Merck's extra pure mandelic acid, thorium nitrate, potassium phosphate ($KH_2PO_4$), potassium iodide, hydrochloric acid and sodium thiosulphate were used. For making solutions bi-distilled water was used.

*Preparation of Thorium Phosphate Gel.*—Thorium phosphate gel was prepared according to the method of Prakash and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 587) by mixing 0·25 c.c. of a solution of potassium phosphate (22·0%) with 5 c.c. of a solution of thorium nitrate (48·14 g./litre), making the total volume in all cases to 6 c.c. The mixtures on shaking for 3 minutes and allowing to stand for 5 minutes gave a transparent, colourless and viscous sol which set to a firm jelly after about 4 hours.

To study the reaction in thorium phosphate gel, the reactants were mixed in thorium phosphate sol and allowed to stand in the dark until the reaction mixture set to a firm and transparent jelly. The "set" reaction mixture was then exposed to monochromatic light.

To study the reaction in thorium phosphate sol, the reactants were mixed in thorium phosphate sol and exposed, just after mixing, to monochromatic light. The reaction was stopped within 72 hours during which the sol did not set to a jelly. In order to prevent the hydrolysis of ferric chloride, a certain amount of hydrochloric acid was added to the solution of ferric chloride.

*Measurement of the Velocity of Reaction.*—Thorium phosphate gel, though thixotropic, liquefies to a very viscous liquid on shaking vigorously and so it was found very difficult to pipette out the exposed reaction mixtures at definite intervals. For this reason 2 c.c. of the reaction mixture were exposed in the reaction cell each time and the whole amount was taken out in a stoppered conical flask after a definite period and the ferric chloride was estimated iodometrically by titrating, in an atmosphere of $CO_2$, with 0·0029*N*-thiosulphate solution by means of a microburette. The initial concentration of ferric chloride was determined in the same way.

The $p_H$ of the reaction mixture was determined potentiometrically by using glass electrode. The $p_H$ of different mixtures were kept constant by adding required quantities of HCl or KOH.

*Measurement of Intensity.*—The intensity of radiation absorbed by the reaction mixture was measured by means of a "Weston's photronic cell" and a sensitive galvanometer. The photronic cell was calibrated by means of a standard lamp (12 v; 4·0W), standardised by means of a Moll thermopile and a Hefner lamp. The intensity of absorbed radiation was measured by noting the deflections when the light passed through (*a*) pure solvent *i.e.*, water or thixotropic thorium phosphate sol or thorium phosphate jelly and (*b*) the reaction mixture. The difference in deflections in the two cases gave the intensity of radiation absorbed by the reaction mixture. It is to be pointed out here that thorium phosphate sol or gel has got no absorption in 366$\mu\mu$.

It was found that the intense yellow colour, produced by mixing mandelic acid with ferric chloride solution in water, became pale yellow in media of thorium phosphate sol and gel. The extinction coefficients of ferric chloride were measured in the three media by means of intensity measurements, keeping the concentration of mandelic acid greater than that of ferric chloride and the ratio $\frac{(\text{Mandelic acid})}{(\text{FeCl}_3)}$ constant. The extinction coefficients at different wave-lengths and different media were found in the following way: The deflections in the galvanometer were noted, first of all, with the solvent alone and secondly with ferric chloride and mandelic acid mixtures of known concentrations. The molecular extinction coefficients of ferric chloride were then calculated according to the equation,

$$\epsilon = \frac{1}{c.d} \log_{10} \frac{I_0}{I_t}.$$

where $\epsilon$ = molecular extinction coefficient,
$c$ = concentration of ferric chloride in g. mols per litre,
$d$ = thickness of the reaction cell in cm. and
$I_0$, $I_t$ are the incident and transmitted radiations measured.

The extinction coefficients of ferric chloride were also measured in presence of varying quantities of thorium nitrate. The results are tabulated in Tables I and II.

TABLE I

| λ | Phase. | ε. | λ. | Phase. | ε. |
|---|---|---|---|---|---|
| 366 $\mu\mu$ | Aqueous | 1629·0 | 436 $\mu\mu$ | Aqueous | 610·3 |
| ,, | Thorium phosphate sol | 106·2 | ,, | Thorium phosphate sol | 47·6 |
| ,, | Thorium phosphate gel | 106·2 | ,, | Thorium phosphate gel | 46·2 |

TABLE II

$a$ = Conc. of ferric chloride in g. mols/litre
$b$ = ,, mandelic acid ,, λ = 366 $\mu\mu$.

$a \times 10^4 = 1·94$ $b \times 10^4 = 2·24$

| | | | | | | |
|---|---|---|---|---|---|---|
| (Thorium nitrate) × $10^4$... | | 2·3 | 6·9 | 13·8 | 20·3 | 33·2 |
| ε ... | 1663·0 | 1173·0 | 739·9 | 565·7 | 438·5 | 366·1 |

From Table II we can see that even small amount of thorium nitrate lowers the extinction coefficients to a great extent.

The reactions which do not take place in the dark were carried out at 25·0°. The experimental data are recorded in Tables III to VII. The reaction was found to be zero-molecular with respect to ferric chloride. In the given tables $\Delta x/\Delta t$=zero-molecular velocity constant=changes in concentration of ferric chloride in 2·0 c.c. reaction mixture per minute in terms of c.c. of 0·0029$N$-thiosulphate.

In the tables $\theta$=temperature; $I_{abs}$=no. of quanta absorbed per c.c. per sec. and $a$ and $b$ have their usual significance as mentioned before.

### TABLE III

*Determination of the order of the reaction,*

Medium=thorium phosphate gel; $\lambda=436$ $\mu\mu$; $\theta=25{\cdot}0^\circ$; $a=6{\cdot}23\times10^{-3}$ $M$; $b=7{\cdot}4\times10^{-3}M$; $I_{abs}=300{\cdot}7\times10^{13}$; $p_H=1{\cdot}74$.

| | Time. | 0·0029$N$-thio for 2 c.c. reaction mixture. | $\Delta x/\Delta t\times10^3$. |
|---|---|---|---|
| 1 | 0 min. | 4·30 | 7·67 (from 1 and 2) |
| 2 | 60 | 3·84 | 7 58 (from 1 and 3) |
| 3 | 120 | 3·39 | 7·63 (mean) |

### TABLE IV

*Effect of varying the concentration of mandelic acid.*

Medium=thorium phosphate gel; $\theta=25^\circ$; $p_H=1{\cdot}74$, $\gamma$=quantum efficiency.

| $\lambda$ ($\mu\mu$) | $a\times10^3$ (mols) | $b\times10^3$ (mols) | $I_{abs}\times10^{-13}$ | $\Delta x/\Delta t.10^3$ | $\frac{\Delta x/\Delta t\ 10^{18}}{I_{abs}}$ | $\gamma$. |
|---|---|---|---|---|---|---|
| 366 | 6·22 | 3·7 | 110·1 | 3·7 | 3·4 | 0·05 |
| ,, | ,, | 7·4 | 120·9 | 4·7 | 3·9 | 0·06 |
| ,, | ,, | 14·8 | 122·2 | 5·3 | 4·4 | 0·07 |
| 436 | 6·23 | 3·7 | 231·9 | 4·0 | 1·7 | 0·03 |
| ,, | ,, | 7·4 | 300 7 | 7·6 | 2·5 | 0·04 |
| ,, | ,, | 11·1 | 339·3 | 9 0 | 2·6 | 0·04 |
| ,, | ,, | 14·8 | 343·7 | 9·5 | 2·8 | 0·04 |

### TABLE V

*Effect of varying the concentration of ferric chloride.*

Medium=thorium phosphate gel; $\theta=25^\circ$; $p_H=1{\cdot}74$.

| $\lambda$ ($\mu\mu$) | $a\times10^3$ (mol) | $b\times.10^3$ (mol) | $I_{abs}\times10^{-13}$ | $\Delta x/\Delta t.10^3$ | $\frac{\Delta x/\Delta t.10^{18}}{I_{abs}}$ | $\gamma$. |
|---|---|---|---|---|---|---|
| 366 | 3·11 | 7·4 | 76·3 | 3·0 | 3·9 | 0·06 |
| ,, | 6·22 | ,, | 120·9 | 4·7 | 3·9 | 0·06 |
| ,, | 9·33 | ,, | 128·5 | 5·2 | 4·0 | 0 06 |
| 436 | 3·11 | 7·4 | 206 2 | 4 6 | 2·2 | 0·03 |
| ,, | 6·22 | ,, | 300·7 | 7·6 | 2·5 | 0·04 |
| ,, | 9 33 | ,, | 355·0 | 8·4 | 2·4 | 0·04 |
| ,, | 12·44 | ,, | 386·8 | 9·0 | 2·3 | 0·03 |

### TABLE VI

*Effect of varying the intensity of absorbed radiation.*

Medium=thorium phosphate gel; $\theta=25^\circ$; $p_H=1{\cdot}74$.

| $\lambda$ ($\mu\mu$) | $a\times10^3$ (mol) | $b\times10^3$ (mol) | $I_{abs}\times10^{-13}$ | $\Delta x/\Delta t.10^3$ | $\frac{\Delta x/\Delta t.10^{18}}{I_{abs}}$ | $\gamma$. |
|---|---|---|---|---|---|---|
| 366 | 6 22 | 7·4 | 120·9 | 4·7 | 3·9 | 0·06 |
| ,, | ,, | ,, | 76·3 | 3·0 | 3·9 | 0·06 |
| 436 | ,, | ,, | 300·7 | 7·6 | 2·5 | 0·04 |
| ,, | ,, | ,, | 186·1 | 5·0 | 2·7 | 0·04 |

### TABLE VII

*Effect of the nature of medium*

$\theta=25^\circ$; $p_H=1{\cdot}74$; $a\times10^3=6{\cdot}227M$; $b\times10^3=7{\cdot}4M$.

| $\lambda$ ($\mu\mu$) | Medium. | $I_{abs}.10^{-13}$ | $\Delta x/\Delta t.10^3$ | $\gamma$. | $\lambda$ ($\mu\mu$) | Medium | $I_{abs}.10^{-13}$ | $\Delta x/\Delta t.10^3$ | $\gamma$. |
|---|---|---|---|---|---|---|---|---|---|
| 366 | Aqueous | 131·0 | 9·5 | 0·11 | 436 | Aqueous | 595·7 | 25·7 | 0·06 |
| ,, | Thorium phosphate sol | 120·9 | 4·5 | 0·06 | ,, | Thorium phosphate sol | 300·7 | 7·6 | 0·04 |
| ,, | Thorium phosphate gel | 120·9 | 4·7 | 0·06 | ,, | Thorium phosphate gel | 300·7 | 7·6 | 0·04 |

## DISCUSSION

The reaction has the following characteristics:

(*a*) The reaction is zero-molecular with respect to ferric chloride. (*b*) The zero-molecular velocity constant increases with increasing concentration of mandelic acid. (*c*) The quantum efficiency is less than unity. (*d*) The zero-molecular velocity constant is directly proportional to the intensity of absorbed radiation. (*e*) The velocity constant increases with increasing concentration of ferric chloride. In fact $\Delta x/\Delta t.10^{18}/I_{abs}$ remains always constant for a particular wave-length but increases with increase in the magnitude of the quanta absorbed. (*f*) The rate of reaction is the same in medium of thorium phosphate sol, before and after gelation, whereas it is much greater in pure water as medium.

On the observations made by Kistler (*J. Phys. Chem.*, 1931, **35**, 815) that the dielectric constants of thixotropic sols remain the same before and after gelation and also on the observations made by Heymann (*Trans. Faraday Soc.*, 1936, **32**, 462) that there is no change in volume of thixotropic sols after gelation so that the average distance between the constituent particles does not alter, we can explain the reason for the same rate of reaction in thorium phosphate sol, before and after gelation, by assuming that the activated ferric ion deactivates to the same extent in media of both thorium phosphate sol and gel.

The quicker reaction in water may be due to a complex formation between mandelic acid and ferric chloride as is evidenced by the deep yellow colour of the mixture.

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# O-ALDEHYDOCARBOXYLIC ACIDS. PART IV. SYNTHESIS OF 5 : 6-METHYLENEDIOXYPHTHALALDEHYDIC ACID

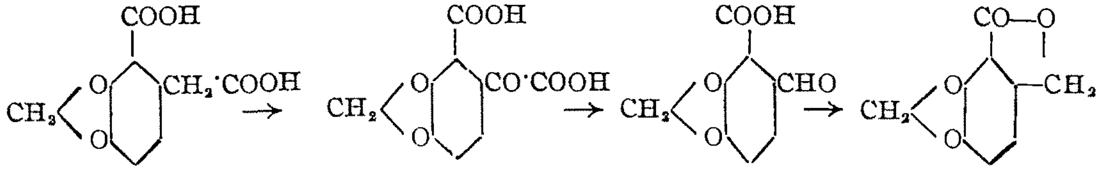
By S. N. Chakravarti

5 : 6-Methylenedioxyphthalaldehydic acid for the synthesis of which numerous attempts have been made including one by Perkin and Trikojus has been synthesised :

5 : 6-Methylenedioxyhomophthalic acid, synthesised by an improved method, was oxidised in boiling xylene solution by means of selenium dioxide to 5 : 6-methylenedioxyphathalonic acid and which was converted into 5 :6-methylenedioxyphthalaldehydic acid, m.p. 155°, through its sodium bisulphite compound. This acid gave on reduction 5 :6-methylenedioxyphathalide, m p 227° and starting from this important acid Cryptopine and Protopine have been synthesised

5 :6-Methylenedioxyphthalaldehydic acid* for the synthesis of which an unsuccessful attempt was made by Perkin and Trikojus (*J. Chem. Soc.*, 1926, 2926) and which has been obtained by Manske by the hydrolysis of bicuculline, an alkaloid occurring in *Corydalis sempervirens* and *Adlumia fungosa* (*Canad. J. Res.*, 1933, **8**, 142) has now been synthesised by methods similar to those employed in the case of opianic acids and 4 : 5-methylenedioxyphthalaldehydic acid (Chakravarti *et al.*, *J. Indian Chem. Soc.*, 1934, **11**, 715, 873 ; 1940, **18**, 264).

5 : 6-Methylenedioxy-homophthalic acid (I) was prepared by a slight modification of the method of Haworth, Perkin and Stevens (*J Chem. Soc.*, 1926, 1764) and oxidised in boiling xylene solution by means of selenium dioxide to 5 : 6-methylenedioxyphthalonic acid (II), which was converted into 5 :6-methylenedioxyphthalaldehydic acid (III), m.p. 155° through its sodium bisulphite compound.



(I) (II) (IV) (IV)

The acid (III) gave on reduction 5 : 6-methylenedioxyphthalide (IV), m.p. 227°.

The further characterisation of this important acid and the synthesis of cryptopine and protopine starting from this acid is reserved for a future communication.

## EXPERIMENTAL

5 : 6-*Methylenedioxyhomophthalic Acid* (I).—Carefully purified β-piperonylpropionic acid, m.p. 87-89°, was brominated in acetic acid medium and the purified bromo-acid cyclised to the corresponding bromohydrindone by the method of Haworth, Perkin and Stevens (*loc. cit.*). The *iso*nitroso derivative of the hydrindone was prepared in the following manner, which is more convenient than the method described by Perkin and co-workers.

The hydrindone (10 g.) was dissolved in hot benzene (50 c.c.) and *iso*amyl nitrite (15 g ) added with stirring. To the mixture concentrated hydrochloric acid (5 c.c.) was added and the whole kept at 50° for an hour when the *iso*nitroso compound gradually separated from the solution in an almost quantitative yield.

---

[* Nomenclature after Beilstein].

The *iso*nitroso derivative was converted into bromopiperonyl nitrile in the following manner.

The *iso*nitroso compound (1·4 g.) was dissolved in sodium hydroxide solution (14 c.c. of 10%) and treated gradually with *p*-toluenesulphonyl chloride (2 g.). The whole mixture was heated for about 15 minutes on the water-bath when a clear solution was obtained. On cooling, the sodium salt of the nitrile, which is rather sparingly soluble in cold water, separated. The precipitated salt was filtered, collected and dissolved in a little hot water and the hot aqueous solution acidified when the nitrile was precipitated in a pure state. More of the nitrile (less pure) was obtained by acidifying the mother-liquor from the first precipitate.

The nitrile was then hydrolysed to 6-bromo-5 : 6-methylenedioxyhomophthalic acid by means of 10% sodium hydroxide and the bromo-acid dehalogenated by the method of Haworth, Perkin and Stevens.

5 : 6-*Methylenedioxyphthalaldehydic Acid* (III).—5 : 6-Methylenedioxyhomophthalic acid (I) (1 g.) was suspended in dry xylene (100 c.c.) and the mixture heated to boiling. Selenium dioxide (0·7 g.) was added to the boiling mixture and the boiling continued for 4 hours, when the homophthalic acid gradually went into solution and a deep red solution containing a black deposit of selenium was obtained. The mixture was thoroughly extracted with dilute sodium carbonate solution and the combined extracts made just acid and evaporated to dryness. The residue was taken up in boiling water, filtered from a little insoluble matter and the filtrate treated with excess of sodium bisulphite solution and evaporated to dryness on a steam bath and then heated for half an hour at 120° in an air-oven. The residue thus obtained was twice stirred up with excess of concentrated hydrochloric acid and the resulting solution evaporated to dryness on a steam bath. This residue was extracted twice with boiling benzene and benzene removed from the combined benzene extract by distillation. The residue (0·4 g.) on repeated crystallisation from water gave 5 : 6-methylenedioxyphthalaldehydic acid as beautiful needles, m.p. 155°. (Found : C, 55·6 ; H, 3·1. $C_9H_6O_5$ requires C, 55·8 ; H, 3·1 per cent). This acid is readily soluble in alcohol, moderately soluble in benzene and very sparingly soluble in petroleum ether.

5 : 6-*Methylenedioxyphthalide.*—The acid (III) (0·3 g.) dissolved in dilute sodium hydroxide solution (10 c.c. of 5%) was reduced with excess of sodium amalgam (10 g. of 4%). The aqueous solution was separated from mercury, filtered, heated to boiling and acidified. On cooling, the phthalide separated in almost theoretical yield as needles, m.p. 227°. (Found : C, 60·5 ; H, 3·6. $C_9H_6O_4$ requires C, 60·7 ; H, 3·4 per cent). The phthalide crystallised readily from water. It is readily soluble in alcohol, sparingly soluble in benzene and almost insoluble in petroleum ether.

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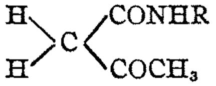
# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART VI, INTERACTION OF NITROSYL CHLORIDE ON SUBSTITUTED AMIDES OF ACETOACETIC ACID

By K. G. Naik, R. K. Trivedi and B. N. Mankad

In order to study the reactivity of the methylene group $-CH_2-$ in the case of the substituted amides of acetoacetic acid, the interaction of nitrosyl chloride with the following substances has been investigated: (i) acetoacetanilide, (ii) acetoacet-*o*-tolylamide, (iii) acetoacet-*p*-tolylamide (iv) acetoacet-1:3:4-xylylamide (v) acetoacet-α-naphthylamide, (vi) acetoacet-β-naphthylamide.

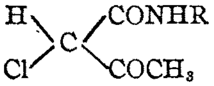
All the above compounds react with nitrosyl chloride yielding their respective yellow *iso*nitroso derivatives (oximes) without giving the corresponding isomers.

The present work was undertaken in the expectation of throwing some light on the relationship between the chemical activity exhibited by and the absorption in the ultraviolet of (1) the various substituted amides of acetoacetic acid, (2) their chloro derivatives and (3) their *iso*nitroso derivatives, which can respectively be generally represented as:



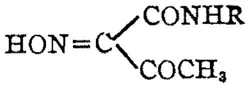
$$\mathrm{H_2C(CONHR)(COCH_3)}$$

(I)



$$\mathrm{HClC(CONHR)(COCH_3)}$$

(II)



$$\mathrm{HON{=}C(CONHR)(COCH_3)}$$

(III)

where R= phenyl, tolyl, xylyl or naphthyl group.

It was proposed to investigate the difference in the absorption in the ultraviolet and the general chemical activity of the amides by transforming the reactive methylene group contained in the compound into -CHCl- and -C=NOH groups, and to publish the results in a series of communications. For this purpose, the following studies have been made:

1. Interaction of the substituted amides of acetoacetic acid with sulphuryl chloride giving monochloro derivatives of the amides.
2. Interaction of the above amides with nitrosyl chloride giving *iso*nitroso derivatives of the amides.
3. The absorption in the ultraviolet of the amides of acetoacetic acid and of their monochloro and *iso*nitroso derivatives.
4. Velocity of hydrolysis of the amides in alkaline and acidic media.
5. Velocity of replacement of chlorine from the -CHCl- group.

The following substances have been selected for the purpose:

*(1) Acetoacetanilide. *(2) Acetoacet-*o*-tolylamide. *(3) Acetoacet-*p*-tolylamide. *(4) Acetoacet-1:3:4-xylylamide. *(5) Acetoacet-α-naphthylamide. *(6) Acetoacet-β-naphthylamide. *(7) Monochloro-acetoacetanilide. (1) Monochloro-acetoacet-1:3:4-xylylamide. (9) Monochloro acetoacet-α-naphthylamide. *(10) *iso*Nitrosoacetoacetanilide. (11) *iso*Nitroso-acetoaeet-*o*-tolylamide. (12) *iso*Nitroso-acetoacet-*p*-tolylamide. (13) *iso*Nitroso-acetoacet-1:3:4-xylylamide. (14) *iso*Nitroso-acetoacet-α-naphthylamide. (15) *iso*Nitroso-acetoacet-β-naphthylamide.

The substances marked (*) in the above list are known. The remaining have been prepare for the first time.

Naik and his collaborators have studied the reactivity of the hydrogen atoms in the case of organic compounds, containing the grouping -$COCH_2.CO$- with different agents, *e.g.* sulphur monochloride, sulphur dichloride, sulphuryl chloride, selenium tetrachloride, thionyl chloride, mercury acetamide, mercury acetate, mercury acetamide, mercury acetate and sulphur dichloride (Naik, *J. Chem. Soc.*, 1921, **119**, 379, 1231, 2592; *J. Indian Chem. Soc*, 1927, **4**, 525; 1926, **3**, 260; 1927, **4**, 11; 1928, **5**, 579; 1930, **7**, 611; 1930, **7**, 655; 1930, **7**, 137; 1932, **9**, 127; 1931, **8**, 29; 1932, **9**, 855; 1932, **9**, 185; 1936, **13**, 25).

However no study of the interaction between the substances of the above mentioned type and nitrosyl chloride has been made. This investigation was, therefore, undertaken to elucidate the reactivity of the methylene group situated between the carbonyl groups and the mode of reactions in the case of substituted amides of acetoacetic acid. It is likely that

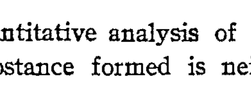
(1) Nitrosyl chloride may act as a chlorinating agent. In this case it would be expected to give either monochloro or dichloro compounds, where the hydrogen atoms of the reactive methylene group may be replaced by chlorine. That nitrosyl chloride does behave as a chlorinating agent is evident from the researches carried out by several investigators (Solanina, *J. Russ. Phys. Chem. Soc.*, 1899, **30**, 437; Tilden, *J. Chem. Soc*, 1895, **67**, 489; Titherely, *ibid.*, 1894, **65**, 521).

(2) Nitrosyl chloride may act as a 'nitrosoing agent' giving rise to nitroso or *iso*nitroso compounds. This mode of reaction has been amply studied by several workers (Tilden, *J. Chem. Soc.*, 1895, **67**, 489; Whiteley, *ibid.*, 1900, **77**, 1040; 1903, **83**, 24; Tsker and Jones, *ibid.*, 1909, **36**, 1910).

(3) It is also possible that nitrosyl chloride may form additive products with unsaturated compounds (*cf.* Tilden, *J. Chem. Soc.*, 1877, **31**, 554; Tonnies, *Ber.*, 1879, **12**, 169; 1887, **20**, 2987; Tilden and Sudborough, *J. Chem. Soc.*, 1893, **63**, 479; Wallach, *Annalen*, 1888, **245**, 245; 1889, **252**, 109; 1889, **253**, 251; 1892, **270**, 174; 1893, **277**, 153; 1904, **332**, 395; 1905, **336**, 12).

Taking into consideration the varied probabilities of the reactions, it was thought interesting to study comprehensively the mode of the reactions, in the case of substituted amides of acetoacetic acid. For that purpose, substances from 1 to 6 have been made to react with nitrosyl chloride. The substances are dissolved in anhydrous benzene and gaseous nitrosyl chloride, prepared by Tilden's method (*loc. cit.*), is passed into the solution until saturation, the flask being surrounded by ice-cold water. It is subsequently refluxed over a water-bath till the solvent is free from gaseous substances and is then allowed to evaporate spontaneously. The product is washed thoroughly with light petroleum and repeatedly crystallised from suitable solvents such as chloroform, light petroleum etc.

That the substances, have the structure :



$$\begin{matrix} CH_3CO \\ RNHCO \end{matrix}\!\!>C=NOH$$

is evident from the following :

The qualitative and the quantitative analysis of the products show the total absence of chlorine proving that the substance formed is neither a monochloro nor an additive product of the amide with the nitrosyl chloride.

(2) The substances form characteristic violet ferrous salts and yellow alkali salts showing the presence of =NOH group (Whiteley, *J. Chem. Soc.*, 1903, **83**, 24). Further, Victor Meyer (*Ber.*, 1877, **10**, 2076) and other workers studied the interaction of nitrous acid on acetoacetic

acid. The product obtained by this interaction is the same as that obtained by Whiteley by the interaction of nitrosyl chloride with ethyl acetoacetate. Knorr (*Annalen*, 1884, **236**, 85) studied the interaction of nitrous acid on acetoacetanilide. He also obtained the *iso*nitroso derivatives of the amide to which he attributed a similar constitution as given by Whiteley.

(3) From the constitution of the original compounds, it appears that the acidic hydrogen in =NOH is furnished by the swinging of the hydrogen atom which formed a part of the group.

(4) The formation of yellow alkali salts is characteristic of α-oximino-ketones to which the oximes under discussion belong.

From the foregoing, it becomes evident that the reaction of nitrosyl chloride on the substituted amides of acetoacetic acid takes place according to the second possibility.

Compounds 11 to 15 were obtained in the above way from compounds 2 to 6, the *iso*nitroso derivatives of acetoacetanilide (1) being already known.

It was expected that substituted amides of acetoacetic acid would give either (1) structural isomers or (2) stereoisomers in the case of their oximes as was shown by Whiteley in the case of the oximes of substituted amides of malonic acid (*loc. cit.*). Contrary to our expectations, however, no such isomers could be isolated inspite of many attempts being made to separate them, if in any case present, by using various solvents. Absence of existence of isomers has also been noted in the case of (1) ethyl acetoacetate (Whiteley, *loc. cit.*), (2) acetyl acetone (Zanetti, *Gazetta*, 23, II, 303), (3) acetoacetanilide (Knorr. *loc. cit.*, (4) cyanoacetic ester and cyanoacetamide (Conrad and Schulze, *Ber.*, 1909, **42**, 735). However, cyanaocetanilide gives two *iso*nitroso derivatives.

From the above, one is led to infer that:—

(1) The effect of aliphatic groups on the formation of isomerides appears to be negative. As stated above, in acetyl acetone, acetoacetic ester, cyanoacetic ester, cyanoacetamide, acetoacetanilide etc., the effect of groups such as $CH_3CO$-, -$OOC_2H_5$, -$CONH_2$, is predominently negative. This is especially so when the groups are asymmetrically situated with respect to carbon to which *iso*nitroso group has been attached. In the case of malonamide, however, where the -$CONH_2$ groups are symmetrically situated with respect to the carbon to which NOH group has been attached, formation of isomers results.

(2) The effect of aromatic groups favours the formation of isomeric oximes, when they are either the only groups in the molecule or they are the predominent groups in the same. In this way the formation of isomerides in the case of cyanoacetanilide can be explained.

(3) When the aromatic groups are balanced by similarly situated aliphatic groups in the same molecule, their effect is counterbalanced by the effect of the latter ones. This fact has been well observed by many workers in this direction. To quote Shriner and others (Gilmann, Org. Chem., Vol. I, p. 390) 'Usually in the aliphatic series only one form can be isolated. Most of the known pairs of isomers have been obtained from aromatic aldehydes and ketones.' It can be added to this that whenever a molecule is a combination of aliphatic and aromatic groups, the formation of isomeric substances would depend upon the balance of the influence of those groups, positive results being obtained if the aromatic groups are the only groups or the most predominating groups in the molecules, and negative results being obtained whenever

the aliphatic groups are the only groups by themselves or when they are sufficiently influential enough to counterbalance the influence of the aromatic part in the molecule.

(4) According to Hantzsch (*Ber.*, 1892, **25**, 2164) different groups exhibit different attractions for the hydroxyl group of the oxime and hence under the circumstances only one form is stable In the present case therefore it is possible to assume that the difference existing between the attractions of the $CH_3CO$- and -CONHR groups on the hydroxyl group of the oxime, may be responsible for preventing the formation of the expected stereoisomers.

## EXPERIMENTAL.

*Interaction of Acetoacetanilide with Sulphuryl Chloride.*—Acetoacetanlide (50 g.) was suspended in anhydrous ether (360 c.c.) cooled in ice-water. Sulphuryl chloride (39 g.) was added dropwise, the solution being mechanically stirred for a quarter of an hour after the sulphuryl chloride was added, when a white precipitate of monochloro-acetoacetanilide separated out. It was filtered under suction and after being thoroughly washed with ether and dry light petroleum was kept over sodium hydroxide under reduced pressure. Finally it was crystallised from alcohol. The other compounds were prepared and purified in a similar way. The properties and analysis of the compounds have been given in Table I.

TABLE I

| Name of the compound. | M.p. | Crystalline structure. | Solubility | Analysis | |
|---|---|---|---|---|---|
| | | | | Found, | Calc. |
| Monochloro-acetoacetanilide | 138° | Needles from alcohol | Highly soluble in benzene, chloroform, carbon tetrachloride, sparingly soluble in alcohol and practically insoluble in ether and light petroleum | Cl, 17·05 | 16·7 |
| Monochloro-acetoacet-1:3·4-xylylamide. | 114° | Plates from 50% alcohol | Do | 14·75 | 14·81 |
| Monochloro-acetoacet-α-naphthylamide | 135° | Needles from alcohol | Do | 13·36 | 13·58 |

*Interaction of Acetoacetanilide with Nitrosyl Chloride.*—Acetoacetanilide (10 g.) was dissolved in dry benzene (100 c.c.), and the mixture was surrounded by ice-water. Dry nitrosyl chloride gas was passed slowly, shaking the whole reaction mixture all the time till the mixture was saturated with nitrosyl chloride. The solution gradually attained yellow colour which tended to deepen and finally assumed a deep reddish yellow colour. It was subsequently refluxed on a water-bath till the evolution of hydrogen chloride gas and the excess of nitrosyl chloride ceased. Spontaneous evaporation of the solution left behind a solid yellow mass which was crystallised from a mixture of five parts of light petroleum and one part of chloroform. The other compounds were prepared and purified in a similar way. The analysis and properties of the compounds have been given in Table II.

TABLE II

| Name of compound. | M.p. | Crystalline structure. | Solubility. | Analysis. Found: | Analysis. Calc. |
|---|---|---|---|---|---|
| *iso*Nitroso-acetoacet-anilide. | 100° | Short prismatic needles. Pale yellow | Soluble in alcohol, acetone benzene, acetone, chloroform carbon tetrachloride; sparinghly in ether; insoluble in light petroleum. | N, 13·97 | 13·59 |
| *iso*Nitroso-acetoacet-*p*-tolylamide. | 92° | Long orange yellow needles | Do<br>except that it is soluble in petroleum. | 12·57 | 12·73 |
| *iso*Nitroso-acetoacet-*o*-tolylamide. | 130° | Long yellow silky needles | ,, | 12·71 | 12·73 |
| *iso*Nitroso-acetoacet-1:3:4-xylylamide. | 145° | Very fine light yellow short needles | ,, | 11·98 | 11·97 |
| *iso*Nitroso-acetoacet-α-naphthylamide. | 138° | Deep yellow tiny needles | ,, | 10·82 | 10·94 |
| *iso*Nitroso-acetoacet-β-naphthylamide. | 152° | Tiny light silky yellow needles | ,, | 10·5 | 10·94 |

The authors are grateful to H. H. the Maharaja Gaekwad's Government for necessary facilities given for carrying out the above work.

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# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART VII. ABSORPTION SPECTRA OF THE AMIDES OF ACETOACETIC ACID

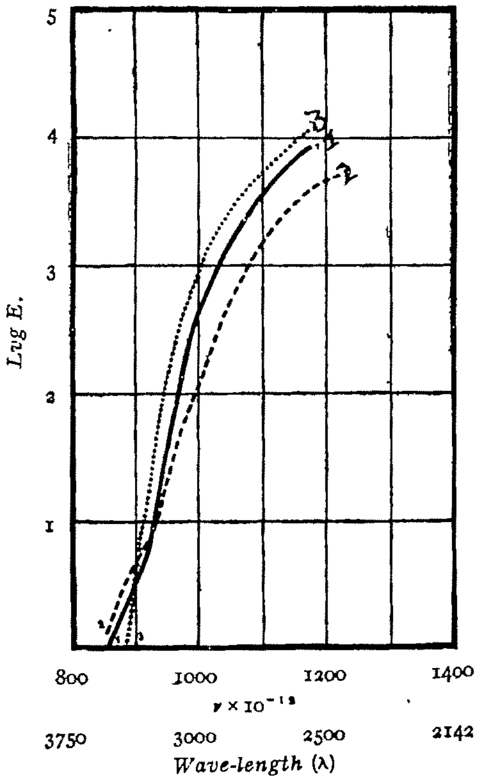
By K. G. Naik, R. K. Trivedi and B. N. Mankad

The following substances have been examined for the absorption spectra in the ultraviolet in aqueous solution : (1) acetoacetanilide, (2) acetoacet-*o*-tolylamide, (3) acetoacet-*p*-tolylamide, (4) acetoacet-1:3:4-xylylamide, (5) acetoacet-*α*-naphthylamide and (6) acetoacet-*β*-naphthylamide.

At the outset the following substituted amides of acetoacetic acid were examined for their absorption spectra in the ultraviolet :—1. Acetoacetanilide 2. Actoacet-*o*-tolylamide. 3. Acetoacet-*p*-tolylamide 4. Acetoacet-1:3:4.-xylylamide 5. Acetoacet-α-naphthylamide 6. Acetoacet-*β*-naphthylamide.

Of these the first three have already been studied by Ramart, Naik and Trivedi (*Bull.*, *Soc. Chim.*, 1934, **1**, 525.) by means of Zeiss spectrograph in alcoholic solution. In Fig. 1 are given the curves as obtained by these workers). The nature of these curves shows that a considerable quantity of the enol form is present in the alcoholic solution. This is especially evident from the fact that the bands due to the ketonic groups are not shown.

FIG. 1



Secondly, the curves show that the presence of methyl groups considerably alters the position of the curves. Again the position of the methyl groups in the nucleus with regard to -NH- grouping also brings about a change in the position of these curves.

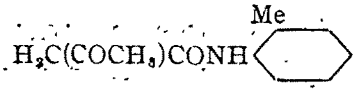
In the present study, alcohol has been replaced by water as a solvent. The curves obtained are shown in Fig. 1.

Two points emerge out clearly with reference to these curves :—

1. The characteristic bands due to the presence of simple ketonic form are observed between the wave-lengths 2800-2400 Å. This must be ascribed to the ketonic structure of the amides persisting in aqueous solution. It is of interest to note that the previous workers, Ramart, Naik and Trivedi (*loc. cit.*) show the presence of enol-form which must be ascribed to the alcoholic solution. It is well-known that such keto-enol transformations depend upon the solvent used.

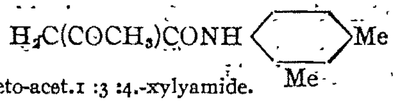
2. The disposition and the direction ef the curves remain the same as in the absorption spectra obtained by Ramart, Naik and Trivedi. It can be said that the total effects of the groups carried by the two carbonyl groups remain the same as in the previous work.

In Fig. 2 is also traced the curve of absorption spectra of acetoacet-2;3:4.xylylamide. It will be seen that there is a close resemblance between these curves and that of the acetoacet-*o*-tolylamide. This must be attributed to the similarity of structures of these two substances as indicated below.



$H_2C(COCH_3)CONH$

Acetoacet *o*-tolyamide



$H_2C(COCH_3)CONH$

Aceto-acet.1 :3 :4.-xylyamide.

The difference in the degree of absorption is due to the presence of $CH_3$-group in *para* position to- NH- group.

FIG. 2

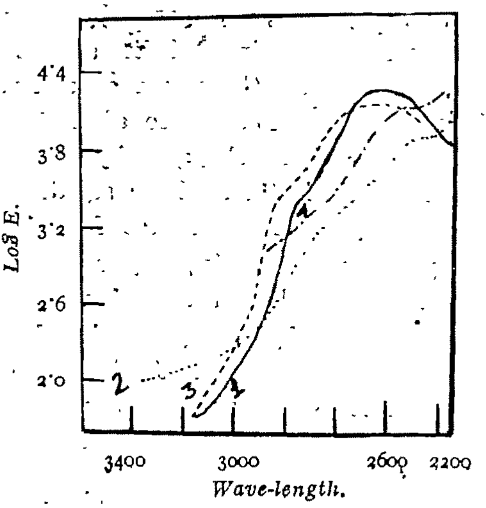


FIG. 3

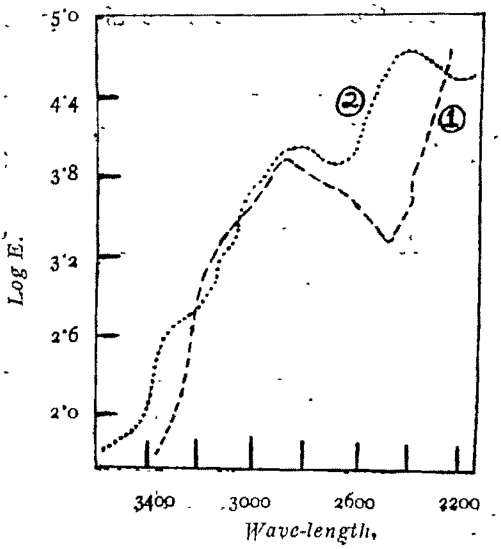


FIG 4

Curves 1—2 refer respectively to α- and β-naphthylamine.

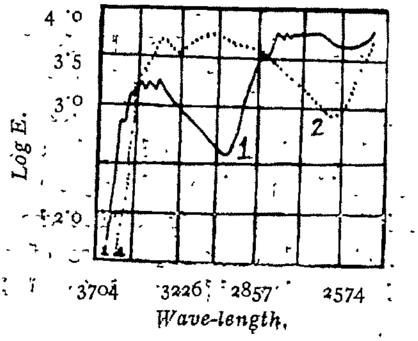
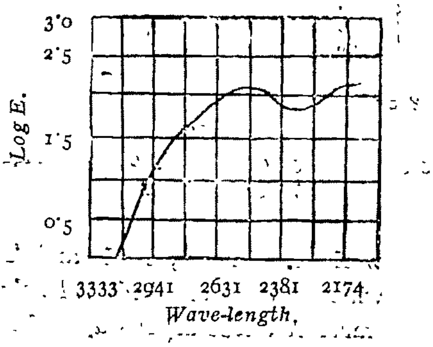


FIG 5



Thus structural similarities are translated by light absorption as represented by the curves.

In Fig. 3 are shown the curves for (1) Acetoacet-α-naphthylamide. (2) Acetoacet-β-naphthylamide.

The bands are characteristics of the naphthyl residue and they also show the peculiarities of the ketonic groups viz. the disposition of the crest between 2800-2400Å. The distinct difference between the curves of α-naphthylamide and β-naphthylamide must be attributed to the structures of their amino residues. Other workers have also observed such differences. Curves for the absorption of α-naphthylamine and β-naphthylamine also exhibit similar difference. (Krüss, *Z. physikal. Chem.*, 1884, **51**, 251) (*vide* Fig. 4).

This point also brings into relief the relationship between absorption spectra and structures of organic substances. This fact is well brought out in relief by reference to the curve of absorption spectra of ethyl acetoacetate itself (Grossmann, *Z. physikal. Chem.*, 1924, **109**, 305) (*vide* Fig. 5). It will be seen that the chief characteristics of curves shown above persist. The difference in disposition of curves is due to the difference in structure, because in all the above cases the ester group, -$COOC_2H_5$ has been replaced by groups such as -CONHR.

The authors are grateful to H.H. the Maharaja Gaekwad's Government for necessary facilities given for carrying out the above work.

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# A NEW METHOD OF FORMATION OF EUDALENE

By Ram Naryan Chakravarti

A synthesis of pure eudalene from 5-methyl-1-keto-1:2:3:4-tetrahydronaphthalene-3-carboxylic acid has been described. The latter has also been prepared by an unambiguous method from 4-methyl-1-hydrindone.

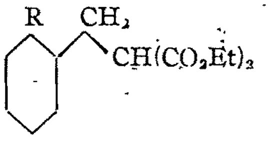
The fundamental naphthalene hydrocarbon eudalene, $C_{14}H_{16}$, first isolated by Ruzicka, Meyer, and Mingazzini (*Helv. Chim Acta*, 1922, **5**, 363) by the dehydrogenation of a number of natural sesquiterpenes has been definitely shown to be 1-methyl-7-*iso*propylnaphthalene by both analytical and synthetical methods (Ruzicka and Mingazzini, *Helv. Chim. Acta*, 1922, **5**, 710 ; Ruzicka and Stoll, *ibid.*, 923). Its important bearing on the sesquiterpene chemistry is now well established (Ruzicka, " Uber Konstitution und Zusammenhänge in der Sesquiterpene reihe", p. 46 ; also Bradfield, Hegde, Rao and Simonsen, *J. Chem. Soc.*, 1936, 672 ; Bradfield, Pritchard and Simonsen, *ibid.*, 1937, 761 ; Bradfield, Penfold and Simonsen, *ibid.*, 1932, 2753 ; Penfold and Simonsen, *ibid* , 1939, 87) and a number of independent syntheses of eudalene are on record (Darzens and Levy, *Compt. rend.*, 1932, **194**, 2056 ; Barnett and Sannders, *J. Chem. Soc.*, 1933, 434).

The present investigation was undertaken with the object of obtaining an authentic specimen of eudalene required in connection with another investigation, since there exists a considerable discrepancy among previous workers regarding the melting points of the solid derivatives of eudalene (see table below).

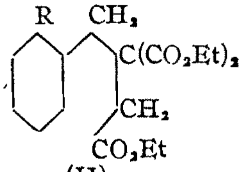
Table I

| Previous authors | Picrate, m.p. | Styphnate, m.p. |
|---|---|---|
| Ruzicka, Meyer and Mingazzini | 90-91° | 119-120° |
| Darzens and Levy | 92·8° | 119·8° |
| Barnett and Sannders | 95° | 122° |
| Bradfield, Hegde, Rao and Simonsen | 91-92° | 117-118° |

The starting point in this synthesis was ethyl *o*-xylylmalonate (I, R = Me) which was condensed with ethyl bromoacetate in presence of sodium ethoxide to give (II, R = Me). The latter on hydrolysis and elimination of carbon dioxide afforded *o*-xylylsuccinic acid (III, R = Me), m.p., 172°, which was characterised by an anhydride, anilic acid, and an anil. With concentrated sulphuric acid the acid underwent cyclisation to 5-methyl-1-keto-1:2:3:4-tetrahydronaphthalene-3-carboxylic acid (IV, R = Me), m.p. 164°.



(I)



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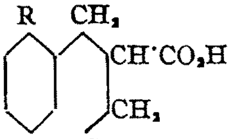
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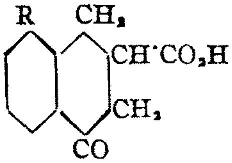
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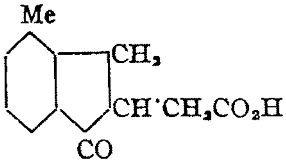
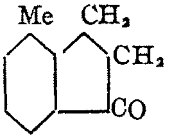
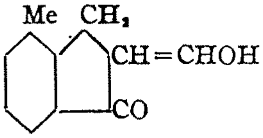

(V)

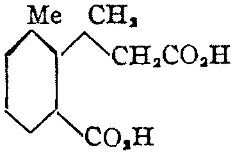
The constitution of (IV, R = Me) is assumed from analogy with cyclisation of benzylsuccinic acid (III, R = H) to the corresponding tetrahydronaphthalene derivative (IV, R = H) (Attwood, Stevenson and Thorpe, *J. Chem. Soc.*, 1923, **123**, 1758 ; *cf.* Von Braun, *Ber.*, 1928, **61B**, 441). It is quite conceivable, however, that it might be the hydrindone (V).

For our purpose, therefore, it seemed desirable to confirm the constitution of the keto-acid (IV, R = Me) by a rational synthesis as follows :—

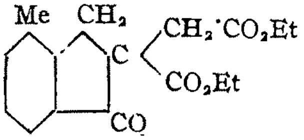
4-Methyl-1-hydrindone (VI) (Young, *Ber.*, 1892, **25**, 2104 ; Mercer and Robertson, *J. Chem. Soc* , 1936, 292 ; Plattner and Wyss, *Helv. Chim. Acta*, 1940, **23**, 907), prepared by an improved method from *β*-*o*-tolylpropionic acid, condenses with ethyl formate in presence of finely divided sodium (*cf.* Bardhan, *J. Chem. Soc.*, 1936, 1851) to give the unstable hydroxymethylene derivative (VII) (*cf.* Ruhemann and Levy, *J. Chem. Soc.*, 1912, 2546) which on successive


(VI)


(VII)


(VIII)

treatment with hydroxylamine hydrochloride and alkali yields the dicarboxylic acid (VIII), m.p. 172° (*cf.* Bardhan, *loc. cit.*, Robinson and Rydon, *J. Chem. Soc.*, 1939, 1401). The diethyl ester of (VIII) on treatment with molecular sodium (Titley, *J. Chem. Soc.*, 1928, 2572) followed by the action of ethyl bromoacetate gives the hydrindone derivative (IX) in an excellent yield. The later on alkaline hydrolysis affords the tricarboxylic acid (X), m.p. 217-18°.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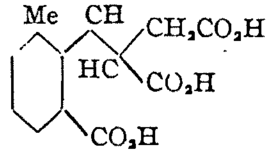
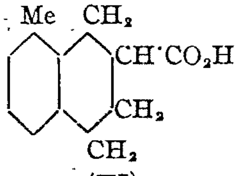
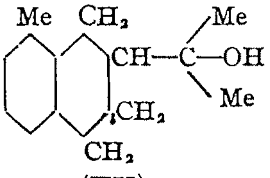

(X)

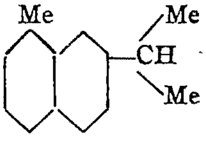
The diethyl ester of (X) on treatment with sodium followed by hydrolysis of the resulting product with dilute hydrochloric acid furnishes a keto-acid, m.p. 164°, indistinguishable from the tetrahydronaphthalene derivative (IV, R = Me) described above.

The keto-acid on Clemmensen's reduction gives an acid (XI), m.p. 132°. The corresponding ester is treated with an excess of magnesium methyl iodide to give the expected tertiary alcohol (XII) having a characteristic terpene-like smell. The latter on dehydroganation with selenium at 230-300° for 24 hours gives eudalene, picrate m.p. 93°, styphnate, m.p. 120° (*cf.* Table I). The regenerated hydrocarbon forms a colourless oil, b. p. 112°/6 mm., $d_4^{20}$, 0·9740 ; $n_D^{20}$, 1·5833 ; $[R_L]_D$, 63·2.

The physical constants are in good agreement with those recorded by Ruzicka and co-workers (*loc. cit.*) for pure eudalene.


(XI)


(XII)


(XIII)

## EXPERIMENTAL

### A. *Synthesis of 5-Methyl-1-keto-1:2:3:4-tetrahydronaphthalene-3-carboxylic Acid* (IV, R=Me)

o-*Xylylmalonic Ester.*—Ethyl malonate (48 g.) was added dropwise to a suspension of finely divided sodium (6·9 g.) in benzene (100 c.c.) and the mixture kept overnight. *o*-Xylyl bromide (55·5 g.) was then added to it and it was refluxed on a steam-bath for 24 hours. The product was then treated with water. The benzene layer was separated, washed and the benzene evaporated. The liquid remaining was then distilled in *vacuo*, b.p. 148°/5 mm., yield 45 g.

*Ethyl* γ-(o-*tolyl*) *propane-*αββ*-tricarboxylate* (II, R=Me).—To an ice-cold solution of sodium (3·34 g.) in absolute alcohol (70 c c.) *o*-xylyl malonic ester (38·3 g.) was added and then ethyl bromoacetate (16·5 c.c.) was added drop by drop and the solution kept overnight. The reaction was completed by heating on the water-bath for 3 hours. After the removal of alcohol, it was diluted with water when a heavy oil separated. It was taken up in ether. The ether solution was washed and concentrated. The residual liquid boiled constantly at 186°/5 mm., yield 47 g. or 92% of theory. (Found : C, 65·0 ; H, 7·4. $C_{19}H_{26}O_6$ requires C, 65·1 ; H, 7·4 per cent).

o-*Xylylsuccinic Acid* (III, R=Me).—The above product (20 g.) was heated on the water-bath for 1 hour with alcoholic potash (30%, 75 c.c.) After the removal of alcohol, it was acidified and kept overnight when a solid acid separated out. It was filtered off, dried on a porous plate and the dry acid heated to 180° in an oil-bath till the evolution of $CO_2$ ceased. The solid residue obtained on cooling was crystallised from water, m. p. 172° with a little previous shrinkage. (Found: C, 64·5 ; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·8 ; H, 6·3 per cent).

The *anhydride*, obtained on heating the acid with acetic anhydride, is a viscous liquid, b p 270°/50 mm. The *anilic acid*, prepared from the anhydride and aniline in benzene solution, crystallises from a mixture of benzene and acetone, m p. 157-58°. (Found : C, 72·4 ; H, 6·3. $C_{18}H_{19}O_3N$ requires C, 72·7 ; H, 6·4 per cent).

On heating the anilic acid to 170° for an hour the *anil* was obtained, which crystallises from dilute alcohol, m.p. 114°. (Found : C, 77·2 ; H, 6·3. $C_{18}H_{17}O_2N$ requires C, 77·4 ; H, 6·1 per cent).

*5-Methyl-1-keto-1:2:3:4-tetrahydronaphthalene-3-carboxylic Acid* (IV, R=Me).—Finely powdered, dry *o*-xylylsuccinic acid (4 g.) was dissolved in concentrated sulphuric acid (20 c.c.) and kept overnight. The solution was then poured on to crushed ice with stirring when *5-Methyl-1-keto-1:2:3:4-tetrahydronaphthalene-3-carboxylic acid* (IV, R=Me) separated out. It crystallises from hot water in colourless shining crystals, m. p. 164°, yield 1 g. (Found : C, 70·2 ; H, 5·8. $C_{12}H_{12}O_3$ requires C, 70·5 ; H, 5·8 per cent).

The *semicarbazone* crystallises from dilute acetic acid, m. p. 255°. (Found: C, 59·2; H, 5·8. $C_{13}H_{15}O_3N_3$ requires C, 59·7; H, 5·7 per cent)

### B. *Rational Synthesis of 5-Methyl-1-keto-1:2:3:4-tetrahydronaphthalene-3-carboxylic Acid* (IV, R=Me) *from 4-Methyl-1-hydrindone*

$\beta$-*o*-Tolylpropionic acid was prepared by hydrolysing *o*-xylylmalonic ester with 25% alcoholic potash. After an hour of refluxing the alcohol was evaporated off with the addition of water and the solution acidified with hydrochloric acid and kept overnight. The separated solid acid was collected, dried and then heated to 160-70° for about 2 hours till the evolution of carbon dioxide ceased. The product obtained on cooling was crystallised from water in thin shining plates, m. p. 103° (melting point given by Young is 102° and by Mercer and Robertson is 104-105°).

*4-Methyl-1-hydrindone* (VI).—The dry acid obtained above (27 g ) was heated to 50° for 1 hour with thionyl chloride (14·5 c.c.). The last traces of thionyl chloride were then removed in *vacuo* at 50-60° and the acid chloride of $\beta$-*o*-tolylpropionic acid (28 g.) was fractionated at 96°/5 mm. Powdered anhydrous aluminium chloride (35 g.) was added in three portions to the acid chloride in dry petroleum ether (80 c.c.), the flask being heated in warm water after each addition and shaken. It was then heated on a water-bath for about 3 hours with frequent shaking, at least half the volume of petroleum ether was allowed to escape through the condenser during this time. It was then decomposed with ice, acidified with hydrochloric acid, and heated on the water-bath for 1 hour. It was cooled and extracted with ether. The ethereal solution was extracted with dilute sodium carbonate solution to remove acidic product. On evaporation of the ether, the solid residue was distilled at 120°/5 mm., yield 12·5 g. 4-Methyl-1-hydrindone (VI) crystallises in fine needles from petroleum ether or dilute acetone, m. p. 101-102°. The yield of (VI) by the cyclisation of *o*-xylylsuccinic acid (III, R=Me) by Young's method (*loc. cit.*) is less than 25% and the m. p. given by him is 95°. Mercer and Robertson (*loc. cit.*) prepared the ketone (m. p. 103-4°) by the cyclisation of the acid chloride in benzene solution but they did not mention the yield. (Found : C, 81·7 ; H, 6·7. $C_{10}H_{10}O$ requires C, 82·1 ; H, 6·8 per cent).

The *phenylhydrazone* crystallises from dilute alcohol in almost colourless crystals which become yellow to orange in presence of light, m.p. 139° (decomp.), m.p. given by Young is 133°. (Found : C, 81·0; H, 6·7. $C_{16}H_{16}N_2$ requires C, 81·3; H, 6·7 per cent).

The *semicarbazone* crystallises from dilute acetic acid decomposing at 260°. (Found: C, 64·6; H, 6·4. $C_{11}H_{13}ON_3$ requires C, 65·0; H, 6·4 per cent).

*1-Methylbenzene-2-* $\beta$-*propionic)-3-carboxylic Acid* (VIII).—The formyl derivative of the methylhydrindone was prepared by adding the ketonic substance (6 g.) to a suspension of finely divided sodium (4 g.) in dry benzene (120 c.c.) and shaken in the cold till it went into solution. Ethyl formate (11 c.c.) was then added and after keeping overnight, it was treated with ice-water, the benzene layer separated and the aqueous layer extracted once with ether. The aqueous solution was then acidified with ice-cold dilute hydrochloric acid when a light yellow precipitate was obtained. It was filtered and washed well with water, yield 6·5 g. It gave a reddish violet colouration with ferric chloride and went into solution in dilute aqueous sodium carbonate or sodium hydroxide with a pink colour. As the hydroxymethylene compound gave difficulty in crystallisation it was directly converted into the cyanoketone.

The above product (6·5 g.) was heated to 70° with glacial acetic acid (300 c.c.) and powdered hydroxylamine hydrochloride (5 g.) was stirred in. After 15 minutes, the solution was cooled, diluted and the orange-red solid filtered, washed well with water and dried on a porous plate. The crude cyanoketone (6 g.), thus obtained, was dissolved in a solution of caustic potash (16 g.) in spirit (16 c.c.), and water (16 c.c.) and heated in a steam-bath for 60 hours and then a further quantity of potash (16 g. in 16 c.c. of water) was added and the heating was continued for 80-90 hours till the evolution of ammonia ceased. The mixture was diluted with water, filtered and the filtrate acidified when an acid was precipitated. This was purified by dissolving in dilute sodium bicarbonate and reprecipitation with acid when the sparingly soluble 1-*methylbenzene*-2-(*β-propionic*)-3-*carboxylic* acid (VIII) was obtained, yield 2·8 g. It crystallised from hot water, m. p. 172°. (Found: C, 63.3; H, 5.7. Equiv., 104·4. $C_{11}H_{12}O_4$ requires C, 63·4; H, 5·7 per cent. Equiv., 104).

The *diethyl ester* was prepared by refluxing the above acid (2·5 g.) for 12-14 hours with absolute alcohol (15 c. c.) and concentrated sulphuric acid (0·75 c. c.). It was then diluted with water and extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution and water. The solvent was then evaporated and the residual liquid distilled at 150°/5 mm., yield 2·55 g. (Found: C, 67·9; H, 7·4. $C_{15}H_{20}O_4$ requires C, 68·1; H, 7·5 per cent).

*The Tricarboxylic Acid* (X).—The above ester (2·4 g.) was heated on the water-bath for 3 hours with finely divided sodium (0·25 g.) in benzene (7 c.c.) when the whole product solidified. It was cooled in ice, ethyl bromoacetate (1·2 c c.) was added and kept overnight. It was then refluxed on the water-bath for 20 hours, cooled and treated with water. The benzene layer was separated. The aqueous layer was extracted once with ether. The benzene-ethereal extract was washed with water and the solvent evaporated. The crude product, thus obtained, was hydrolysed by heating on a water-bath for 3 hours with 20% alcoholic potash. The alcohol was then evaporated with the addition of water. After separation of any neutral impurity present by extraction with ether, the aqueous solution was acidified when the acid (X) was precipitated, yield 1·9 g. It crystallises from hot water, m.p. 217-18°. (Found: C, 58·2; H, 5·2. $C_{13}H_{12}O_6$ requires C, 58·6; H, 5·2 per cent).

The *ethyl ester* of the above tricarboxylic acid was prepared by heating the dry acid (1·5 g.) on the water-bath for 20 hours with absolute alcohol (10 c.c.) and concentrated sulphuric acid (0.75 c.c.). It was then worked up and distilled in the usual way. It boils at 178°/4 mm., yield 1·45 g. (Found: C, 64·8; H, 7·2. $C_{19}H_{26}O_6$ requires C, 65·1; H, 7·4 per cent).

5-*Methyl*-1-*keto*-1:2:3:4-*tetrahydronaphthalene*-3-*carboxylic Acid* (IV, R=Me).—The above tri-ethyl ester (1·35 g.) was heated on the water-bath for 4 hours with molecular sodium (0·1 g.) in benzene (5 c.c.). It was then cooled, treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed and the benzene evaporated. The residual oil was then hydrolysed by refluxing on a sand-bath for 15 hours with excess of 6% hydrochloric acid. The solution was then neutralised with soda and extracted with ether to remove some neutral matter. The aqueous solution was then acidified when a crystalline acid was precipitated. After two crystallisations from hot water it melted at 164°. No depression of the m p. took place on mixing it with the keto-acid obtained by the cyclisation of *o*-xylylsuccinic acid with concentrated sulphuric acid. (Found: C, 70·3; H, 5·8. $C_{12}H_{12}O_3$ requires C, 70·5; H, 5·8 per cent).

### C. *Synthesis of* 1-*Methyl*-7-iso*propylnaphthalene* (*Eudalene*)

5-*Methyl*-1:2:3:4-*tetrahydronaphthalene*-3-*carboxylic Acid* (XI).—The keto-acid (IV, R=Me) (4·7 g.) was heated on a sand-bath for 40 hours with concentrated hydrochloric acid (40 c.c.) and amalgamated granulated zinc (35 g.). It was diluted with water, extracted with ether and the soild residue (3·6 g.) obtained on evaporation of the ether crystallised from water in fine needles, m.p. 132°. (Found: C, 75·6 ; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75.8 ; H, 7.3 per cent).

The *ethyl ester* was prepared in the usual way by heating the acid (6.1 g.) on the water-bath for 10-12 hours with absolute alcohol (40 c.c.) and concentrated sulphuric acid (3 c.c.). It was then diluted with water and the separated oil taken up in ether. The ethereal solution was washed with dilute sodium carbonate solution and water, and dried over anhydrous calcium chloride. The solvent was then evaporated. The residual liquid boiled constantly at 132°/4 mm., yield 5·9 g. (Found: C, 76·7 ; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·0 ; H, 8·2 per cent).

*The Alcohol* (XII).—The above ester (5·7 g.) in dry ether (10 c.c) was added drop by drop to ice-cold methyl magnesium iodide, prepared from magnesium filings (1·9 g.), methyl iodide (5·6 c.c ) and dry ether (40 c.c.). It was kept overnight and then refluxed for 1 hour with shaking from time to time. It was decomposed with crushed ice and acidified with ice-cold dilute sulphuric acid. The ethereal layer was separated and the aqueous portion extracted with ether. The ether was then evaporated and the residual viscous liquid (5 g.) was heated on a water-bath for 1 hour with 10% alcoholic caustic potash to hydrolyse any unchanged ester. The alcohol was evaporated off with the addition of water. The alkaline solution was extracted with ether and the ether evaporated after drying the extract over anhydrous sodium sulphate. The residual oil was distilled in *vacuo* when a highly viscous sweet-scented liquid was obtained boiling at 145°/5 mm., yield 4·5 g. (Found: C, 81·8 ; H, 9·8. $C_{14}H_{20}O$ requires C, 82·3 ; H, 9·8 per cent).

*Eudalene* (XIII).—The above alcohol (4 g.) was heated in a nitrate-bath with selenium (5 g.), the temperature of the bath being gradually raised from 230° to 300° during 24 hours. When cold, the product was taken up in ether and the ethereal solution filtered and dried. The ether was then evaporated, the residual liquid heated for 1 hour at 240° over sodium under reduced pressure and distilled when eudalene was obtained as a colourless liquid, b.p. 109°/5 mm., yield 2·8 g. It was converted into its *picrate*[*], orange-yellow needles, m.p. 93°. (Found: C, 57·8 ; H, 4·6. $C_{20}H_{19}O_7N_3$ requires C, 58·1 ; H, 4·6 per cent).

*Pure* eudalene was obtained by decomposing the picrate with dilute ammonia and extracting the liberated oil with ether. The residual liquid obtained on evaporation of the solvent boiled constantly at 112°/6 mm. (Found : C, 90·8 ; H, 8·66. $C_{14}H_{16}$ requires C, 91·3 ; H, 8·69 per cent). It had $d_4^{20}$, 0·9740 ; $n_D^{20}$, 1·5833 ; $[R_L]_D$, 63·2.

The *styphnate* was readily obtained by heating for a few minutes an alcoholic solution of styphnic acid and eudalene in theoretical quantities. It crystallises from spirit in yellow needles, m.p. 120°. (Found : C, 55·8; H, 4·4. $C_{20}H_{19}O_8N_3$ requires C, 55·9 ; H, 4·4 per cent).

My best thanks are due to Dr. J. C. Bardhan for the facilities given to me and for his keen interest during the progress of the work.

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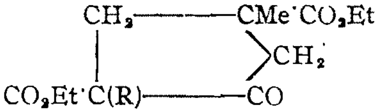
[*] The picrate, m.p. 92°, has also been prepared by Chatterjee and Bose (*J. Indian Chem. Soc* , 1941, 18, 2[illegible]) by a different route.

# THE ACTION OF SODIUM ON ETHYL β-METHYLBUTANE -αβδ-TRICARBOXYLATE. PART V

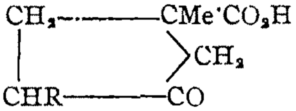
By Ram Narayan Chakravarti

The product of the sodium condensation of ethyl β-methylbutane-αβδ-tricarboxylate consists exclusively of ethyl 3-methyl*cyclo*pentan-1-one-3.5-dicarboxylate, since it can be converted into *cis* 1-methyl*cyclo*pentane-1:3 dicarboxylic acid unaccompanied by 1-methyl*cyclo*pentane-1 2-dicarboxylic acid.

In previous parts of this series (Chakravarti, *J. Indian Chem. Soc.*, 1943, **20**, 173, 189, 247) it has been shown that the product of the action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate on treatment with appropriate reagents *in situ* furnishes the *cyclo*pentanone ester (I, R = Me, Et, -CH$_2$·CO$_2$Et). The proof of the structure of (I) rests on the fact that on hydrolysis it gives either a tricarboxylic acid (II) or a ketonic acid (III) depending on the experimental conditions used.



(I)

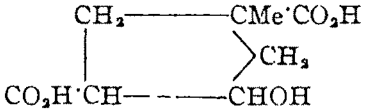


(III)

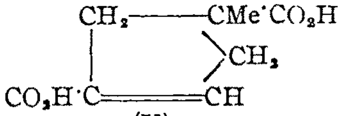
$$CO_2H\cdot CHR\cdot CH_2\cdot CMe(CO_2H)\cdot CH_2\cdot CO_2H$$

(II)

In conformity with this view, the parent ester should possess the structure (I, R = H), since on reduction with sodium amalgam it gives the hydroxy-acid (IV). The ester of (IV) on treatment with phosphorus oxychloride and pyridine and subsequent hydrolysis yields the unsaturated acid (V), m.p. 168°.

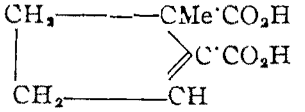


(IV)

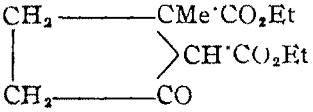


(V)

In spite of careful search, however, no trace of the isomeric unsaturated acid (VI), m.p. 204°, (*cf.* Datta, *J. Indian Chem. Soc.*, 1940, **17**, 611), which is expected to be formed if the Dieckmann product had the alternative structure (VII) suggested by Baker (*J. Chem. Soc.*, 1931, 1548), could be detected.



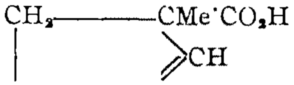
(VI)



(VII)

The acid (V) on hydrogenation in presence of platinum oxide furnishes a mixture of saturated acids from which pure *cis*-1-methyl*cyclo*pentane-1:3-dicarboxylic acid, m.p. 96-97°, has been isolated through its anhydride, m.p. 81° (Toivonen, John, Sainio and Kunsinen, *Suomen*

*Kem.*, 1935, **8**, [B], 46 ; Toivonen, Veijola and Friberg, *ibid.*, 44). For the purpose of direct comparison, however, both the *cis*- and *trans*-modifications of 1-methyl*cyclo*pentane-1:3-dicarboxylic acid have been prepared from ethyl 3-methyl*cyclo*pentan-1-one-3 carboxylate (ester of III, R = H). The latter gives a cyanohydrin (Chakravarti, *J. Indian Chem. Soc.*, 19 3, **20**, 246) which on dehydration and hydrolysis affords a mixture of isomeric products (V) and (VIII) m.p. 155-62°, which could not be separated. The mixture of acids, m.p. 155-62°, on catalytic hydrogenation yields *cis*-and *trans* modifications of 1-methyl*cyclo*pentane-1:3-dicarboxylic acid melting at 96-97° and 114°respectively (*cf.* Toivonen, *loc. cit.*).



(VIII)

It follows therefore that the action of sodium on ethyl β-methylbutane-αβδ tricarboxylate leads to the formation of ethyl 3-methyl*cyclo*pentan-1-one-3:5-dicarboxylate (I, R = H).

The study of the influence of substituents on the course of such reactions is in progress.

## EXPERIMENTAL

### *Conversion of the Dieckmann Product* (I, R = H) *into* cis *1-methyl* cyclo*pentane-1:3-dicarboxylic Acid*

*Reduction of the Dieckmann Product* (I, R = H) *with Sodium Amalgam: Formation of 3-Oxy-1-methyl*cyclo*pentane-1: 4-dicarboxylic Acid* (IV).—The product of sodium condensation of ethyl β-methylbutane-αβδ-tricarboxylate (Chakravarti, *loc. cit.*) was treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed with water, dried over calcium chloride and the benzene evaporated. The residual oil was then distilled in *vacuo*, b.p. 127°/3 mm.

To the above product (6 g.) dissolved in aqueous alcohol, stirred and cooled, sodium amalgam (200 g.) was added during 24 hours. During the course of the reduction a current of $CO_2$ was passed through the solution. After the reduction was complete the aqueous solution was acidified with hydrochloric acid, evaporated to dryness and the residue extracted with ether. The dry gummy product (5 g.), obtained on evaporation of the ether, was esterified by heating on a water-bath for 12 hours with absolute alcohol (20 c.c.) and concentrated sulphuric acid (1·5 c.c.). It was finally diluted with water and extracted with ether. The ethereal extract was washed with dilute sodium carbonate solution and water and the solvent was then evaporated. The residual liquid on distillation gave *ethyl 3-oxy-1-methyl*cyclo*pentane-1:4-dicarboxylate*, b.p. 145°/5 mm., yield 3 g. (Found : C, 58·6; H, 8·0. $C_{12}H_{20}O_5$ requires C, 59·0 ; H, 8·19 per cent).

*Dehydration of the Hydroxy-ester* (as IV) : *Formation of 1-Methyl-*$\Delta^8$-cyclo*pentene-1:3-dicarboxylic Acid* (V) *by Hydrolysis of the Product.*—The above hydroxy ester (2·7 g.) was heated to 140-145° for 1 hour with phosphorous oxychloride (10 c.c.) and dry pyridine (40 c.c ). It was then cooled in ice, decomposed with ice-water, acidified with hydrochloric acid, saturated with salt and extracted with ether. The crude oil obtained on evaporation of the ether was hydrolysed by heating on the water-bath for 1 hour with 10% aqueous alcoholic potash (60 c.c.).

The alcohol was then evaporated off with the addition of water and the solution acidified with hydrochloric acid when the sparingly soluble unsaturated acid gradually separated out, yield 1 g. After one crystallisation from water (using charcoal) it melted at 168°. (Found: C, 56·1 ; H, 5·87. $C_8H_{10}O_4$ requires C, 56·4; H, 5·88 per cent).

*Catalytic Reduction of the above Unsaturated Acid: Formation of 1-Methyl*cyclo*pentane-1:3-dicarboxylic Acid.*—The above acid (0·6 g.) was reduced by shaking in an atmosphere of hydrogen in acetic acid solution in presence of platinum oxide (0·05 g.). 98 C.c. of hydrogen were absorbed in 10 minutes at 28° and then the absorption stopped completely. The solution was then filtered and the acetic acid evaporated off completely. The dry solid (0·5 g.) was treated with acetyl chloride (1 c.c.) and kept overnight. It was then evaporated to dryness in a vacuum desiccator over caustic potash. The finely powdered residue was cooled to 0° and treated with cold 5% sodium carbonate solution. After five minutes it was filtered and crystallised (0·28 g.) from petroleum ether in small colourless needles, m.p. 81°, undepressed when admixed with the *anhydride* of cis-*1-methyl*cyclo*pentane-1: 3-dicarboxylic acid* prepared through the cyanohydrin of 3-methyl*cyclo*pentan-1-one-3-carboxylate (ester of III, R=H). (Found: C, 62·2 ; H, 6·6. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5 per cent).

The pure anhydride was hydrolysed by heating with water and evaporating the clear solution. The residue, thus obtained, crystallised from water and was found to be identical with cis-*1-methyl*cyclo*pentane-1:3-dicarboxylic acid*, m.p. 96-97°, mixed melting point with the authentic sample of the *cis*-acid (*vide infra*).

The sodium carbonate extract on acidification gave an acid too small in quantity to be identified with the *trans*-acid.

### *Synthesis of* cis- *and* trans-*1-Methyl*cyclo*pentane-1:3-dicarboxylic Acid from Ethyl 3-Methyl*cyclo*pentan-1-one-3-carboxylate (Ester of* III, R=H)

Ethyl 3-methyl*cyclo*pentan-1-one-3-carboxylate, required for the purpose, was obtained according to Ruzicka by the sodium condensation of ethyl β-methylbutane-αβδ-tricarboxylate and hydrolysis and subsequent esterification of the condensation product.

*Cyanohydrin of ethyl 3-Methyl*cyclo*pentan-1-one-3-carboxylate* was prepared by adding the above keto-ester (5 g.) drop by drop to cold liquid hydrogen cyanide, obtained by treating potassium cyanide (10 g.) with sulphuric acid (10 c.c. conc. acid and 10 c.c. water), the condensation being brought about in presence of a drop of potassium cyanide solution. It was then kept overnight at a low temperature. The cyanohydrin formed was stabilised by adding a drop of concentrated sulphuric acid and the excess of hydrogen cyanide was removed under suction.

*Dehydration and Hydrolysis of the Cyanohydrin : Formation of a Mixture of* (V) *and* (VIII).—The crude cyanohydrin, obtained above, was refluxed in an oil-bath at 140-45° for 1 hour with phosphorous oxychloride (23 c.c.) and pyridine (84 c.c.). Excess of oxychloride was decomposed by cooling in ice and adding ice-water drop by drop. The solution was then acidified with concentrated hydrochloric acid (45 c.c.) and extracted with ether. The ethereal solution was washed with water and the ether evaporated. The residual unsaturated nitrile was hydrolysed by heating on the sand-bath for 24 hours with concentrated hydrochloric acid (60 c.c.). The sparingly soluble unsaturated acid was then obtained by filtering the cold solution, yield 3 g. It is soluble in hot water and crystallises slowly on cooling, m.p. 155-62°.

The acid, thus obtained, is probably a mixture of (V) and (VIII). (Found: C, 56·2; H, 5·8. $C_8H_{10}O_4$ requires C, 56·4 ; H, 5·88 per cent).

cis-*and* trans-1-*Methyl*cyclo*pentane*-1: 3-*dicarboxylic Acid*.—The above product (2·04 g.) was dissolved in glacial acetic acid (35 c.c.) and shaken with platinum oxide (0·05 g.) in an atmosphere of pure hydrogen under normal pressure and at the room temperature (27°). 320 C.c. of hydrogen (cal. 318 c.c.) were absorbed in 20 minutes. The acetic acid solution was filtered and the acetic acid evaporated off completely (last traces in *vacuo* over caustic potash). The crude acid, thus obtained, was treated with acetyl chloride (3 c.c.) and kept overnight. It was then evaporated to dryness in *vacuuo* over caustic potash. The solid product (1·2 g.) was finely powdered, added to 5% sodium carbonate solution at 0° and after 5 minutes filtered and the *anhydride* of cis-1-*methyl*cyclo*pentane*-1:3-*dicarboxylic acid* crystallised from ligroin in small needles, m.p. 81° (0·85 g.). (Found: C, 62·0; H, 6·5. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5 per cent).

The sodium carbonate extract, obtained above, was acidified with hydrochloric acid and evaporated to dryness on the water-bath. The residue was extracted with ether and the ether evaporated when an impure acid (0·25 g.) was obtained. From this *pure* trans-1-*methyl*cyclo*pentane*-1:3-*dicarboxylic acid*, m.p. 114°, was obtained after repeated crystallisations from water.

The *pure cis*-anhydride (0·4 g.) was hydrolysed by heating with water on a sand-bath for 1 hour when a clear solution was obtained. It was then evaporated to dryness and the residue crystallised from water when *pure* cis-1-*methyl*cyclo*pentane*-1:3-*dicarboxylic acid* was obtained, m.p. 96-97°. (Found : C, 55·5; H, 6·9. $C_8H_{12}O_4$ requires C, 55·8; H, 6·9 per cent).

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# OIL FROM THE SEEDS OF *BOMBAX MALABARICUM*

By C. Venkata Rao, M. Narasinga Rao and A. Venkateswarlu

The oil from the seeds of *Bombax malabaricum* contains 94·8% insoluble mixed fatty acids composed of 57% of solid acids and 43% of liquid acids. The composition of the fatty acids is found to be 1·2% myristic acid, 23·6% palmitic acid, 2·8% arachidic acid, 64·9% oleic acid and 7·5% linoleic acid. The seed cake is found to contain 34·4% of crude protein.

*Bombax malabaricum* belonging to the family of *Bombacacea* is an evergreen tree found in the forest areas in India.

The Kapok, usually mentioned as white silk cotton and red silk cotton, has its origin from distinct genera Buonopozenne (*Eriodendron anfractuosum*) and *Bombax malabaricum*.

Earlier work on the subject deals with the characteristics of Kapok oil without reference to the particular species (Lewkowitsch " Technology and Analysis of Oils, Fats and Waxes ", Vol. II, p. 186; *Bull. Imp. Inst.*, 1926, **24**, 18). Georgi (*Malay Agric. J.*, 1922, **10**, 284) determined the constants of the oil obtained from the seed of *Eriodnedron* species. Latest work done by Mehlebacher (*Oil & Soap*, 1937, **14**, 118) refers to analysis of a sample of refined Kapok oil obtained from Japan. He detected the presence of oleic and linoloic acids in the oil.

As the information on the various constituents of the oil from the seeds of *Bombax malabaricum* is very meagre and a few characterisations found for the oil appear in the common name of Kapok, systematic investigation on the fatty acid composition of the oil was undertaken and the results recorded in this paper.

## EXPERIMENTAL

The seeds of *Bombax malabaricum* were collected in the months of April and May, 1942 from the Parvatipur Agency tract, Vizagapatam, Madras Presidency and the powdered seed on extraction with carbon tetrachloride gave 26% of a dark yellow oil having the physical and chemical characteristics given in Tables I and II along with the figures of analysis of the previous workers.

The present sample has a lower iodine value compared to the sample reported by Sprinkmeyer which might be due to the climatic conditions (*Chem. Umchau*, 1929, **36**, 40). Maumene test indicates that the oil is a non-drying oil which is further corroborated by its low iodine value. The present sample has a high acid value (32·58% as oleic acid), which might be due to the fact that the seeds collected in May were crushed and extracted in December. The oil also develops acidity very rapidly since the value increases from 32·58 to 42·16 in six months. High acid value indicates the ease with which it becomes rancid due to decomposition. This rapid decomposition makes it unsuitable as a frying fat for edible purposes due to the acrid taste and bad odour imparted to the articles fried in this oil. It is noticeable that the acidity increases at a fairly rapid rate, presumbably because of the free acid acting as a catalyst to accelerate the reaction.

TABLE I

*Analysis of the seed*

| | Present workers (Bombax). | Bull. Imp. Institute, (Kapok seed oil). | Georgi (*Eriodendron anfractuosum*). |
|---|---|---|---|
| Ash % seeds | 5·16 | — | — |
| Oil % seeds | 26 | 22·3 | 19·4 to 24·4 |
| Protein % seed cake | 34·4 | 36 | 24·88 |
| Hull % seeds | 45 | — | 43·2 |
| Kernel % seeds | 55 | — | 56·8 |

TABLE II

*Analysis of the oil*

| | Present workers (Bombax). | Lewkowitsch Vol. II Sprinkmeyer (Bombax). | Georgi (*Eriodendron anfractuosum*). | Mehlenbacher (Kapok oil, Japan.) |
|---|---|---|---|---|
| M.p. | 34° | — | — | |
| S. p. | 30° | — | — | |
| Sp. gr. | 0 9362 at 35° | 0·9236 at 15° | 0·918 at 15 5° | 0·920 at 15° |
| Ref. Index | 1·4611 at 40° | 59·7 at 40° Oleo-ref. reading | na 20-1·4685 1·4710 | 57 6 at 40° (Butyro ref. reading) |
| Sap. V. | 196·3 | 194·5 | 191-193·3 | 191·2 |
| I. V. | 68·11 | 93·78 | 94·3-98·1 | 100·5 |
| Acidity | 32·58% as oleic acid | — | 1 8-26·9% | 26·8 |
| Non-sap % | 1·761% | | 8-1·16% | |
| Hehner value | 94·8% | 95·66 | | |
| Maumene test | 133·3 | | | |
| (*b*) *Mixed acids* | | | | |
| Sap. value | 274 5 | | 284·3-292·4 | |
| I. V. | 71·78 | 98·9 | 94·2-96·6 | |

*Component Fatty Acids*

300 G. of the oil were saponified with strong alcoholic soda. The acids liberated from the soap were resolved into solid and liquid acids according to Twitchell's lead-salt-alcohol method (Twitchell, *Ind. Eng. Chem.*, 1921, **13**, 806) and converted into their methyl esters. The physical and chemical properties of the acids and their esters are given below.

TABLE III

| | % on oil. | Sap. equiv. | I. V. |
|---|---|---|---|
| Oil | 100 | 285·8 | 68·1 |
| Mixed acids | 94·8 | 274·5 | 71·80 |
| (S) Solid acids | 54 | 273·5 | 53·1 |
| (L) Liquid acids | 40·8 | 278·9 | 96·9 |
| (S) Solid esters | | 286·8 | 50·6 |
| (L) Liquid esters | | 293·8 | 92·29 |

TABLE IV

*Fractionation of solid esters*

(Wt=85 g.) Sp Eq. 286·8, I.V.=50·6.

| Fr. No. | Temp. bath. | Temp. frac. | Wt. of frac. | Sap. equiv. | I.V. | Identification. |
|---|---|---|---|---|---|---|
| $S_1$ | 190-195° | 136-144° | 10·4 g. | 278·9 | 31·2 | Oleic and palmitic |
| $S_2$ | 195-200° | 144-145° | 35·5 | 283·7 | 47·70 | ,, ,, |
| $S_3$ | 200-205° | 145° | 18·9 | 288·9 | 67·60 | ,, ,, |
| $S_4$ | 205-225° | 145-156° | 12·7 | 296·7 | 61·80 | ,, ,, arachidic |
| $S_5$ | (Residue) | | 7·5 | 296.8 | 34 20 | ,, ,, ,, |

Methyl esters were fractionally distilled at 2 mm. using Willstätter's bulb and the data given in Table IV.

TABLE V

*Fractionation of the liquid esters*

(Wt. = 64 g.) Sap. equiv. 293·2, I.V. = 92·19.

| Frac. No. | Bath temp. | Frac temp. | Frac. wt. | Sap. equiv | I. V. | Identification. |
|---|---|---|---|---|---|---|
| $L_1$ | 190-195° | 99-144° | 12·8 | 285·8 | 65·50 | Oleic, myristic and palmitic |
| $L_2$ | 195-200° | 144° | 13·8 | 292 | 95·80 | Oleic, linoleic and palmitic |
| $L_3$ | 200-215° | 144-150° | 19·5 | 293·3 | 110·5 | ,, ,, |
| $L_4$ | 215-230° | 150-156° | 9·8 | 295·5 | 91·80 | Oleic and linoleic. |
| Residue | | | 8·1 | 302·6* | 87·90 | Oleic and linoleic and non saponifiable matter. |

* Corr. value = 295·8

Myristic acid (m.p. 52°), palmitic acid (m.p. 62°) and arachidic acid (m.p. 75°) were identified from the various fractions by mixed melting points with authentic samples. Methyl arachidate melted at 52-53°. The unsaturated acids were identified by oxidation with alkaline permanganate (Lapworth and Mottram, *J. Chem. Soc.*, 1925, 1628), when dihydroxystearic acid (m.p. 150°) and tetrahydroxystearic acid (m.p. 170-71°) were obtained confirming the presence of oleic and linoleic acids.

Oleic and linoleic acids were further identified by bromination by the method of Eibner and Muganthaller and this indicated the absence of linolenic acid as no hexabromide could be isolated.

From the above identifications the acids are calculated on percentage basis and given below along with the fatty acid composition of cotton seed oil.

TABLE VI

| Acids | Solid 57% | Liquid 43% | Total acids (% by wt.) | Mol. % | *Cotton seed oil, I.V. = 105 |
|---|---|---|---|---|---|
| Myristic | — | 1·2 | 1·2 | 1·45 | 2·3 |
| Palmitic | 20·3 | 3·3 | 23·6 | 25·40 | 24·5 |
| Stearic | — | — | — | — | 1·1 |
| Arachidic | 2·8 | — | 2·6 | 2·50 | 0·5 |
| Oleic | 33·9 | 31·0 | 64·9 | 63·30 | 22·5 |
| Linoleic | — | 7·5 | 7·5 | 7·40 | 46·5 |
| Tetradecenoic | — | — | — | — | 0·2 |
| Hexadecenoic | — | — | — | — | 2·2 |
| | | | 100·0 | 100·00 | 99·8 |

Association ratio = 2·41

* Hilditch and Maddison, *J. Soc. Chem. Ind.*, 1940, 59, 1127.

## CONCLUSIONS

The fatty oil contains 1·2% myristic acid, 23·6% palmitic acid, 2·8% arachidic acid, 64·9% oleic acid and 7·5% linoleic acid. The presence of even traces of stearic acid could not be found.

The seed cake after extraction of the oil is found to contain 34·4% of crude protein, and the ash contains potash. Though adverse reports are made as regards its use as cattle food it should serve as a rich manure.

As the oil develops rapidly free acidity up to 40%, the glyceride structure could not be determined.

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# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART VIII. ABSORPTION SPECTRA OF MONOCHLORO DERIVATIVES OF THE AMIDES OF ACETOACETIC ACID

By K. G. Naik, R. K. Trivedi and B. N. Mankad

Changes in light absorption have been studied by replacing hydrogen atoms of the central methylene group of the following compounds:

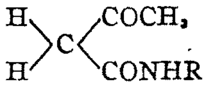
(1) Monochloroacetoacetanilide, (2) monochloroacetoacet-1:3:4-xylylamide, (3) monochloroacetoacet-α-naphthylamide.

Comparing the curves of these chloro derivatives with those of the non-substituted amides, it is found that in the case of the chloro-derivatives: (*i*) the degree of light absorption increases, (*ii*) the curves are shifted towards the visible.

In order to study the change taking place in light absorption when the structure of the amides is altered by replacing the hydrogen atoms of the central methylene group, the following compounds have been studied:

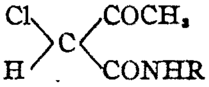
1. Monochloroacetoacetanilide.
2. Monochloroacetoacet-1:3:4-xylylamide.
3. Monochloroacetoacet-α-naphthylamide.

The difference between the structure of the amides and their chloro derivatives is as under



$$\begin{matrix}H\\H\end{matrix}\!>\!C\!<\!\begin{matrix}COCH_3\\CONHR\end{matrix}$$

(I)



$$\begin{matrix}Cl\\H\end{matrix}\!>\!C\!<\!\begin{matrix}COCH_3\\CONHR\end{matrix}$$

(II)

The methylene group ($-CH_2-$), situated between two carbonyl groups, has been transformed into $-CHCl-$. It was expected that such a transformation of the group should

Fig. 1

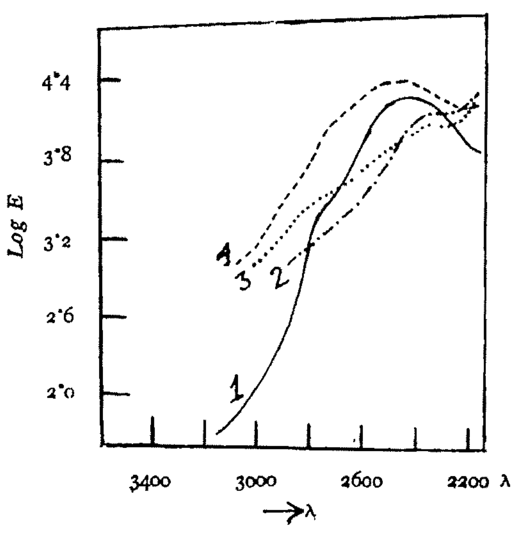
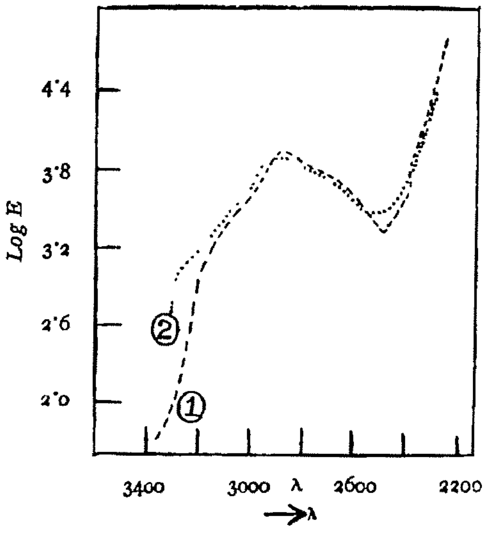


Fig. 2



bring about a change in light absorption. This expectation has been amply realised in the present study.

On Fig. 1 have been traced the curves of :—

(1) Acetoacetanilide.
(2) Acetoacet-1:3:4-xylylamide.
(3) Monochloroacetoacet-1:3:4-xylylamide.
(4) Monochloroacetoacetanilide.

On comparison of the curves of the non-substituted amides with those of the respective chloro-amides it will be seen that, in the case of chlorocompounds (*i*) the degree of light absorption increases, and (*ii*) the curves are shifted towards the visible region. Similar observations have also been made by Mme. Ramart, Naik and Mehta (*J. Indian Chem. Soc.*, 1938, **15**, 421).

In Fig. 2 are traced the curves of

(1) Acetoacet-α-naphthylamide.
(2) Monochloroacetoacet-α-naphthylamide.

Observations similar to those made above can be made in this case too.

From all these it can be said that the sum-total effect of the transformation of -$CH_2$- to -CHCl- group is to increase the degree of absorption, as also to shift the curves towards the visible. The peculiar position and nature of each curve depend upon the position and heaviness of radicals attached to the carbonyl groups. It may also be pointed out that generally the heavier the radical, the greater the shifting of the absorption curves towards the visible. The absorption curves of tolylamides illustrate the difference in the position of the curve due to the proximity or distance of the methyl group, to or from the original amino group.

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# MAGNETIC SUSCEPTIBILITY AND THE CONSTITUTION OF NITROSO-PENTAMMINE COBALT SALTS

By Sailaja Prasad Ghosh and Priyadaranjan Rây

In view of the conflicting values of the magnetic moment of nitroso-pentammine cobalt chloride (black) reported by different investigators, the susceptibility value of this substance, as well as that of its isomeric red complex, was redetermined on very carefully prepared specimens. The black chloride gave a paramagnetic moment of 1·5 Bohr magnetons, whereas the red nitrate was diamagnetic as already reported by previous workers. The value for the black chloride was somewhat lower than that obtained by Milward and co-workers (1·66 Bohr). On the basis of Pauling's structure for NO molecule with a three electron bond, $N\overset{\cdot\cdot\cdot}{=}O$, it has been suggested that the black nitroso-pentammine cobalt complex is an equilibrium mixture of the normal and the excited states of the sixfold, octahedral, penetration complex of bivalent cobalt.

$$[(H_3N)_5.Co: N\overset{\cdot\cdot\cdot}{=}O]^{++}.$$

The spin of the promoted electron in such a complex with hybrid $d^2$-s-$p^3$ bonds may be either parallel or antiparallel to that of the odd electron in the three electron bond of the NO-molecule, representing the normal and the excited state of the molecule respectively. The former corresponds to a triplet paramagnetic state and the latter to a singlet diamagnetic one. This view satisfactorily accounts for the observed magnetic moment. The idea of resonance between a univalent and a tervalent cobalt atom, as put forward by Milward and co-workers, has been shown to be untenable. The red isomer has been proved to contain tervalent cobalt with a monomeric formula as previously shown by Milward and co-workers.

The constitution of the two series (black and red) of isomeric nitroso-pentammine cobalt complex, $[(H_3N)_5.Co.NO]X_2$, has been the subject of much discussion by several workers since their preparation by Sand and Genssler (*Ber.*, 1903, **36**, 2083; *Annalen*, 1903, **329**, 194). Of these the black variety is rather unstable and passes readily with partial decomposition into the stable red modification. The black salts are immediately decomposed by acids and bases with formation of $NH_3$, NO and cobaltous salts, while the red compounds are not attacked by water and dilute acids. With concentrated HCl or HBr, however, the red salts give chloro- or bromo-pentammine cobaltic salts under conditions, which do not permit of any probable oxidation. Werner and Karrer (*Helv. Chim. Acta*, 1918, **1**, 54) studied these compounds more thoroughly and concluded that in the black salts cobalt is present in the bivalent state, whereas in the red forms it is tervalent with NO behaving as a hyponitrite acid radical $(N_2O_2)''$, though no free hyponitrous acid could be isolated. Rây and Bhar (*J. Indian Chem. Soc.*, 1928, **5**, 497), from a measurement of the magnetic susceptibility of the black chloride and the red nitrate, came to the same conclusion; because they found the former paramagnetic, resembling all cobaltous compounds, and the latter diamagnetic like all cobaltic complexes. The authors, therefore, assumed after Werner and Karrer that in the red salts the NO-group is present as an anion of hyponitrous acid serving as a bridge between two tervalent cobalt atoms and giving rise to a dimeric formula,

$$[(H_3N)_5\,Co\text{-}N_2O_2\text{-}Co(NH_3)_5]X_4.$$

A detailed discussion about the structure of the black series, possessing obviously a simple or monomeric formula, was not given by the authors as the specimen employed for susceptibility measurements was not believed to be magnetically pure. They simply suggested the possibility of the black salts being an equilibrium mixture.

Since the development of the quantum mechanical theory of valency much interest has centred round the structure of the stable odd molecule NO with an uneven number of electrons and of the various types of complex [illegible]s containing this molecule, such as nitroso-carbonyls, nitroprusside, salts of chloro- [illegible] nitroso-ruthenium ammines besides the substances under discussion.

Pauling (*J. Amer. Chem. Soc.*, [illegible]25) has shown that the normal state of NO-molecule is best represented by a structu[illegible]ree electron bond, such as $:N\overset{...}{=}O:$, resulting from resonance or interaction between $:N$[illegible] $:N::\dot{O}:^+$. A three electron bond is shown to have half the strength of a single [illegible] properties of the molecule, notably its paramagnetic susceptibility, dipole moment, s[illegible] the internuclear distance, which lie between those for double and triple bonds, are b[illegible]ed for on this view. But he found it rather difficult to give a satisfactory representati[illegible]tructure of the black nitroso-pentammine cobalt salts on this basis. This was ma[illegible] the fact that he assumed the cobalt atom to be tervalent in the black salts.

Milward, Wardlaw and Way (*J. Che*[illegible]38, 233) have made a very careful measurement of the susceptibilities of these two [illegible]omplexes and have obtained a moment value of practically 1·73 Bohr magnetons for the black chloride, and a diamagnetic $\chi_g$-value of $-0{\cdot}11 \times 10^{-6}$ and $-0{\cdot}19 \times 10^{-6}$ for the red nitrate in fair agreement with that given by Rây and Bhar.

Soon after and almost simultaneously, Fraser and Long (*J. Chem. Phys.*, 1938, 462) determined the susceptibility of the black chloride. The $\chi_g$-value obtained by them $(23{\cdot}1 \times 10^{-6})$ gives a magnetic moment of about 3·65 Bohr magnetons for the cobalt atom, rather a very high value compared with that of Milward and co-workers.

It was, therefore, considered desirable to repeat the measurement on the perfectly pure specimens of these two interesting compounds. Details of the preparation and measurement are given below in the experimental part. A value of about 1·5 Bohr magnetons was found for the black chloride. For the red nitrate a diamagnetic gram susceptibility of about $-0{\cdot}20 \times 10^{-6}$ was obtained. The value for the black chloride approaches that of Milward and co workers, although somewhat lower. We are, however, convinced of the purity of our product, and the error of our magnetic measurement cannot possibly exceed 2%.

A problem now presents itself regarding the structure of the black chloride. On the basis of the moment value of about 1·73 Bohr, which should result from the presence of one unpaired electron if spin alone be effective, Milward and co-workers suggested the following resonating structures for this compound :

$$\underset{\text{(I)}}{[(H_3N)_5\overset{\circ}{Co}-\overset{+}{N}\equiv\overset{+}{O}]Cl_2} \quad \text{and} \quad \underset{\text{(II)}}{[(H_3N)_5.\overset{-}{Co}=\overset{+}{N}=O]Cl_2},$$

the NO-group in the molecule being responsible for the resonance. The authors based their view on the findings of Brockway and Anderson (*Trans. Faraday Soc.*, 1937, **33**, 1233), who investigated by electron diffraction the structure of nitroso-carbonyls of cobalt and iron. The metal nitrogen distance in these compounds was found to be somewhat less than the sum of their single bond radius and the internuclear distance of the nitroso-group was intermediate between those for double and triple bonds. Brockway and Anderson, therefore, represented the nitrosyl metal carbonyls in accordance with the resonating electronic structures

$$\overset{\circ}{M}-\overset{+}{N}\equiv\overset{+}{O} \quad \text{and} \quad \overset{-}{M}=\overset{+}{N}=O$$

Milward and co-workers assume that the bivalent cobalt atom in I becomes univalent by receiving an electron from the nitrogen atom of the NO-group, which then co-ordinates with the metal atom by sharing a pair of its own electrons. In structure II, it is believed that a normal co-valency is formed between the cobalt and the nitrogen atom in which each atom contributes one electron to the shared pair besides the co-ordination bond due to a pair of electrons supplied by the nitrogen atom. The primary valency of the cobalt atom in this case changes to three. Such an explanation is far from a happy one. In the first place, two structures having univalent and tervalent cobalt respectively cannot resonate as they do not possess the same number of unpaired electrons, which is one of the fundamental conditions for resonance. Secondly, if we assume that they have the same number of electrons, their magnetic moments must be the same.

The moment value of 3·65 Bohr magnetons for the black chloride, obtained by Fraser and Long, is too high and need not be seriously considered. The authors themselves are doubtful about its correctness, and attribute the high value to possible errors in measurement due to the employment of a weak field and also to the presence of 5 mols of water of hydration in their specimen. It is well-known that the black chloride is very unstable in the moist state and changes readily with decomposition into the red form.

It is, however, difficult to choose between the values of 1·66 Bohr magnetons reported by Milward and co-workers and 1·5 Bohr obtained by us. The former represents the concordant results of measurement on different and presumably pure specimens of the substance extending over a wide range of temperature, −195° to 85°; the latter was based on the measurement of the purest specimen possible.

If we accept Pauling's structure for NO-molecule with a three electron bond, the structure of the black complex can be represented as $[(H_3N)_5.Co{:}N\overset{\cdot\cdot\cdot}{=}O{:}]^{++}$; the Co−N bond may also share a double bond character by resonance, if an unshared pair of electrons from one of the 3-d orbitals of the Co atom is utilised for the formation of an additional co-ordination bond. We have already seen that the cobalt is obviously in the cobaltous state in this octahedral sixfold complex. If this be of the penetration type with $d^2$-$s$-$p^3$ hybrid bonds, then one of the 3-d electrons must be promoted to the 4-d level (*cf.* Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367) in order to make two 3-d orbitals available for bond formation. This will evidently increase the energy of the molecule, and, it is well known, all cobaltous complexes of the penetration type are mostly unstable. This promoted and unbalanced electron may have its spin either parallel or anti-parallel to that of the odd electron of the three electron bond in the NO-group. In the former case the molecule will have a paramagnetic moment of 2·82 Bohr magnetons corresponding to the presence of two unpaired electrons, if spin alone be effective and the orbital moments be completely quenched by interaction with the field of neighbouring atoms and ions. In the latter it will be diamagnetic. Both these states, triplet and singlet, are possible, one representing the normal and the other the excited state of the molecule. The energy difference between the two states in an unstable molecule like this may not, however, be great, and both may exist side by side giving rise to an equilibrium depending upon temperature, influence of light, method of its preparation and purity of the product. A high $\theta$-correction or temperature variation of the magnetic moment of the black chloride, observed by Milward and co-workers, furnishes an evidence in support of this view. The molecule may accordingly give an intermediate moment value of 1·7 to 1·5 Bohr magnetons as actually observed by Milward and co-workers, as well as by ourselves.

The diamagnetic character of the red salt can be easily explained on the basis of a tervalent cobalt in the complex, resulting from the transference of an electron from bivalent cobalt to the nitrogen atom of the NO-group. T[redacted] behaves as an electronegative radical like $CN^-$ or $Cl^-$ and forms a negative $NO^-$ [redacted]en coordinates with the central cobalt atom by sharing a pair of its own electrons. [redacted]ointed out by Milward and co-workers it is therefore no longer necessary to assume [redacted]ula for the red salt.

## EX[redacted]NTAL

*Nitroso-pentammine Cobalt Chl*[redacted].—Schering's nickel-free cobalt chloride (12 g.) was dissol[redacted]. of water and cooled in ice. This was added to about 60 c.[redacted]oled concentrated ammonia. The mixture was then filtered. [redacted] was introduced into the funnel A of Kapsenberg's filterin[redacted] (Fig. 1) from which air was previously replaced by pure n[redacted] The gas was passed through the solution for about three hours. The entire apparatus was kept cooled by wrapping it with a piece of cloth soaked constantly with ice-water. A large quantity of shining black crystals of the compound separated from the solution. The current of NO was stopped after about three hours and a stream of $H_2$-gas was introduced through B. The mother-liquor was then removed by filtration, applying suction at C. The crystals were now washed successively with cold absolute alcohol and dry ether (over met. Na) introduced through E. The crystals were dried on the filter-bed in the current of hydrogen. The product was kept in a stoppered weighing bottle over $CaCl_2$ in a desiccator placed inside a refrigerator. {Found : N, 34·21 ; Co, 24·13 ; Cl, 28·87. $[ON.Co\text{-}(NH_3)_5]Cl_2$ requires N, 34·30 ; Co, 24·08 ; Cl, 29·0 per cent}. $D_4^{30°} = 1\cdot7380$.

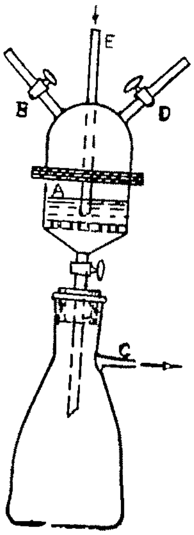

FIG. 1

The substance decomposes in water with evolution of oxides of nitrogen and separation of cobaltous hydroxide. In moist air-free $CO_2$ it changes slowly into pink cobaltous carbonate and ammonium chloride. When treated with water in the absence of air, blue cobaltous hydroxide is produced.

### *Magnetic Susceptibility*

Susceptibility measurements were made according to Guoy's method in a magnetic balance with a maximum field of $10\cdot16 \times 10^3$ Gauss produced by a saturation current of 5 amperes. The substance was weighed in a specially designed glass-stoppered tube. The description of the measurement tube, details of the magnetic balance and the method of measurement were given in a previous paper (*cf.* Rây and Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 323).

The mass susceptibility was calculated according to the formula:

$$\chi_g = \frac{2l \times m'}{m \times H^2 \times 1\cdot019} + \chi_v^T / d_s$$

where $l$ = length of the column of the substance in the tube in cm.,

$m$ = weight of the substance in g.,

$H$ = maximum field strength in gauss,

$m'$ = change in weight in milligrams of the substance,

$d_s$ = density of the substance,

$\chi_v$ = volume susceptibility of air,

$T$ = temperature of measurement (absolute).

$$\chi_{TV} = \frac{2\cdot52 \times 10^{-3}}{T^2}.$$

In the present experiment :—

$$l = 10\cdot7,\ m' = 4\cdot27,\ m = 0\cdot3013,\ H = 10\cdot16 \times 10^3,\ d_s = 1\cdot738,\ T = 301.$$

Hence $\chi_g = 2\cdot885 \times 10^{-6} + 0\cdot016 \times 10^{-6}$ (air) $= 2\cdot901 \times 10^{-6}$.

and $\chi_M = 2\cdot901 \times 10^{-6} \times 245 = 710\cdot7 \times 10^{-6}$.

Correction for diamagnetism :—

$-\chi_a \times 10^{+6}$......$Co^{++} = 12\cdot8$, $Cl^- = 22\cdot0$, (corrected Pascal's value).

$NH_3 = 15\cdot0$ (from corrected Pascal's value of N and H).

$NO = 10\cdot2$ (from corrected Pascal's value of N and $O^-$).

The value for $Co^{++}$ has been assumed to be equal to that for $Zn^{++}$ (as given by Kido's measurement, because of approximate equality of their ionic radii.

The total diamagnetic correction $= +142\cdot0 \times 10^{-6}$. We have not considered any constitutive correction for the complex formation itself as has been done by Milward and co-workers. This is a factor of doubtful value.

Therefore, $\chi_A = (710\cdot7 + 142\cdot0) \times 10^{-6} = 852\cdot7 \times 10^{-6}$. Hence $\mu_B = 2\cdot84\sqrt{852\cdot7 \times 10^{-6} \times 301}$ $= 1\cdot44$.

If $\theta$-correction of -39·9, as given by Milward and co-workers, is inserted, $\mu_B$ becomes 1·53.

The value found by Milward and co-workers is $\mu_W = 8\cdot32$ or $\mu_B = 1\cdot664$.

*Nitroso-pentammine Cobalt Nitrate (red)*.—Cobalt nitrate (17·5 g.) was dissolved in 22 c.c. of boiling water and then treated with 80 c.c. of concentrated ammonia. The mixture was left in the cold for 12 hours and then a stream of pure NO was passed through it in absence of air. The red crystals, that separated, were filtered and recrystallised twice from hot water. The product was finally dried in air. {Found: N, 36·93 ; Co, 19·23. $[ON.Co.(NH_3)_5](NO_3)_2, 0\cdot5\ H_2O$ requires N, 36·48 ; Co, 19·21 per cent.}

*Magnetic susceptibility*

| $l$ | $m'$ | $m$ | $\chi_g \times 10^6$ | |
|---|---|---|---|---|
| 9·2 cm. | 1·50 mg. | 1·306g | −0·2010 | *cf.* $\chi_g \times 10^6 = -0\cdot109$ (Rây and Bhar). |
| 8·3 ,, | 1·23 ,, | 0·9694g | −0·2004 | and −0·19 and −0·11 (Milward and co-workers). |

The values correspond to measurement in air at the room temperature (28°).

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# RELATIONS BETWEEN CHEMICA[redacted]VITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAI NIC MOLECULES. PART IX. ABSORPTION SPECTRA NITROSO DERIVATIVES OF THE AMIDES ETOACETIC ACID

By K. G. Naik, R.[redacted]di and B. N. Mankad

The effect of complete transformation [redacted] $CH_2$·CO– group into –CO·C:NOH·CO– in the following compounds on absorption in the u s been studied: (1) *iso*nitrosoacetoacetanilide, (2) *iso*nitrosoacetoacet-*p*-tolylamide, (3) *iso*nitrosoa -xylylamide.

In order to study the changes b[redacted]t in light absorption when there is complete transformation of the -CO·$CH_2$·CO- gr CO·C:NOH·CO- the following substances have been examined in the ultraviolet.

1. *iso*Nitrosoacet[redacted]
2. *iso*Nitrosoacet[redacted]et-*p*-tolylamide.
3. *iso*Nitrosoacetoacet-1:3:4-xylylamide.

The difference between the structure of the amides and their *iso*nitroso derivatives is

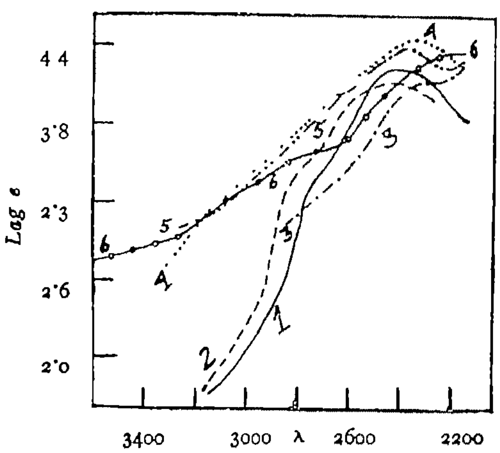
$CH_3CO·CH_2·CONHR$. $CH_3COC(=NOH)·CONHR$.

It is apparent that in the case of *iso*nitroso derivatives there is a total change brought about by the introduction of a double bond in the original -CO·$CH_2$·CO- complex.

The introduction of a double bond brings about an entirely different energy condition in the molecule. This is translated by increased light absorption and by a totally different disposition of curves of absorption.

In Fig. 1 are traced the curves of absorption spectra of (1) Acetoacetanilide. (2) Acetoacet-*p*-tolylamide. (3) Acetoacet-1:3:4-xylylamide. (4) *iso*Nitrosoacetoacetanilide. (5) *iso*Nitrosoacetoacet-*p*-tolylamide. (6) *iso*Nitrosoacetoacet-1:3:4-xylylamide.

Fig. 1



It is apparent from the curves, that:—(*i*) The bands have been conspicuously shifted towards the visible. This can be expected from the very colour of the substances as also from the condition of strain established by the double bond in the molecule. (*ii*) The crests of the curves in the case of the *iso*nitroso compounds have been practically smoothened out, due to change of structure. (*iii*) Other characteristics due to the groups which persist unchanged, are still shown by the curves. (*iv*) The relative position of the curves remains always the same. (*v*) The bases of curves have a tendency to be shifted towards the visible, as also there is a marked sign with regard to a general flattening of the curves.

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# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART X. VELOCITY OF HYDROLYSIS OF SUBSTITUTED AMIDES OF ACETOACETIC ACID

By R. K. Trivedi and B. N. Mankad

The substituted amides of acetoacetic acid have been hydrolysed with a standard solution of (*i*) alcoholic potassium hydroxide, (*ii*) aqueous hydrochloric acid in order to study the rate of hydrolysis in alkaline and acid media.

The following observations have been made in this connection: (*i*) Velocity of hydrolysis (especially alkaline) agrees with their absorption spectra, and appears to depend upon the nature of the radicals attached to the hydrolysable imino group, the position of the methyl group with respect to the imino group and the molecular weight of the radicals attached to the imino group. (*ii*) Introduction of asymmetry increases the relative rate of hydrolysis.

The substituted amides of acetoacetic acid mentioned below have been hydrolysed with a standared solution of (*i*) alcoholic potassium hydroxide (*ii*) aqueous hydrochloric acid, in order to study the rate of hydrolysis in alkaline and acid media.

*1. Acetoacetanilide. *2. Acetoacet-*o*-tolylamide. *3. Acetoacet-*p*-tolylamide.
4. Acetoacet-1:3:4.-xylylamide. 5. Acetoacet-α-naphthylamide. 6. Acetoacet-β-naphthylmide.

The substances marked (*) had been studied by Mme. Ramart, Naik and Trivedi (*Bull. Soc. Chim.*, 1934, **1**, 525) at a concentration other than that adopted in this work.

The aim of undertaking the work embodied in this part is :—

(*i*) To correlate the phase of chemical activity of the molecules expressed by the rate of hydrolysis with their absorption spectra.

(*ii*) To investigate the several factors which govern the chemical activity of these molecules as expressed by the rate of hydrolysis.

The rate of hydrolysis would depend on :—

(*a*) The nature of the grouping -NHR, according as R is phenyl, tolyl, xylyl, or naphthyl group.

(*b*) The position of the alkyl group or groups, in the case of tolyl and xylyl group attached to the nitrogen.

(*c*) The molecular weight and the molecular volume of the groups attached to the -CO- group in the above compounds.

(*d*) The position of -NH- grouping, either α or β, as in the case of naphthylamides.

*The Rate of Hydrolysis in Alkaline Medium.*—The general scheme according to which hydrolysis takes place can be represented as

$$CH_2(COCH_3)\cdot CONHR + KOH \rightarrow CH_2(COCH_3)CO_2K + RNH_2$$

As regards the mechanism of the hydrolysis, Rice states :—

"It may be assumed that the hydrolysis of amides follows a mechanism similar to reactions in which an ester is hydrolysed" (Rice, "Mechanism of Homogeneous Organic Reactions" p. 121).

Accordingly, three essential stages of hydrolysis may be represented thus ;—

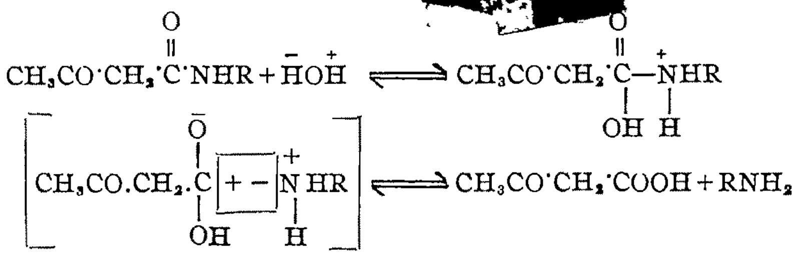
(*i*) Addition of $H_2O$ to the anilide to form a complex ion.

(*ii*) Collision with hydroxyl ion or hydrogen ion, when an alkali or acid is used as a catalyst.

(*iii*) Rupture of the bond by flow of electrons.

In case of an ester, it has been maintained by some authors that the ester first forms a complex ion with H or OH and these ions afterwards collide with the water molecules. In any case, however, during hydrolysis, the [illegible] as regards the complex formation in the system, has been confirmed by majority of investigators.

With these views as the basis, the mechanism of hydrolysis in the present case may be represented thus :—



$$CH_3CO{\cdot}CH_2{\cdot}\overset{\overset{O}{\|}}{C}{\cdot}NHR + \overset{-}{H}O\overset{+}{H} \rightleftharpoons CH_3CO{\cdot}CH_2{\cdot}\underset{OH}{\overset{\overset{O}{\|}}{C}}-\underset{H}{\overset{+}{N}}HR$$

$$\left[CH_3CO.CH_2.\underset{OH}{\overset{\overset{\bar{O}}{|}}{C}}\boxed{+\,-}\underset{H}{\overset{+}{N}}HR\right] \rightleftharpoons CH_3CO{\cdot}CH_2{\cdot}COOH + RNH_2$$

The following method was employed for this investigation.

In each experiment a weighed quantity of 0·01 g.-mol. of the substance was added to 100 c.c. of $N/15$ alcoholic potassium hydroxide solution so as to make the ultimate concentration of the solution 0·1 g.-mol. per litre. Ten ampoules, each containing 5 c c. of the above reacting mixture were placed in a boiling-water-bath at a known time. At the end of every hour, one of the ampoules was withdrawn and the contents were titrated with standard sulphuric acid ($N/60$). For every set two operations were carried out.

The results of the study of hydrolysis have been represented graphically and the summary of the results is given in Table I.

TABLE I

| | Percentage hydrolysed of | | | | | |
|---|---|---|---|---|---|---|
| Time of heating. | Acetoacet-anilide. | Acetoacet-*o*-tolylamide. | Acetoacet-*p*-tolylamide. | Acetoacet-1:3:4-xylylamide | Acetoacet-*a*-naphthyl-amide. | Acetoacet-*β*-naphthyl-amide. |
| 1 hrs. | 10·25 | 12·92 | 12·08 | 11·42 | 15·08 | 12·08 |
| 2 | 19·16 | 20·83 | 20·58 | 21·30 | 22·33 | 20·16 |
| 3 | 26·41 | 28·42 | 27·83 | 27·83 | 31·83 | 28·58 |
| 4 | 31·41 | 33·10 | 34·91 | 32·50 | 34·16 | 32·83 |
| 5 | 35·66 | 36·30 | 36·91 | 36·75 | 36·83 | 35·08 |
| 6 | 38·16 | 38·30 | 38·91 | 37·66 | 39·08 | 36·83 |

In Fig. 1 are traced the curves showing the velocity of hydrolysis of (1) acetoacet-anilide, (2) acetoacet-*o*-tolylamide, (3) acetoacet-*p*-tolylamide, (4) acetoacet-1:3:4-xylylamide.

It will be seen from comparison of these curves with the respective curves of the absorption spectra that the curve for hydrolysis for (3) lies above that of (1) in the same position and sense, as their corresponding absorption curves do. The velocity curve of (2) actually cuts that of (3) and tends to cut that of (1) as reaction proceeds. The curve for absorption spectra of (2) shows a similar tendency. The curve for (4) has not maintained the same position as

FIG. 1

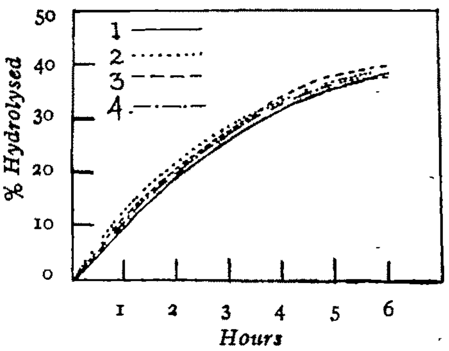


FIG. 2

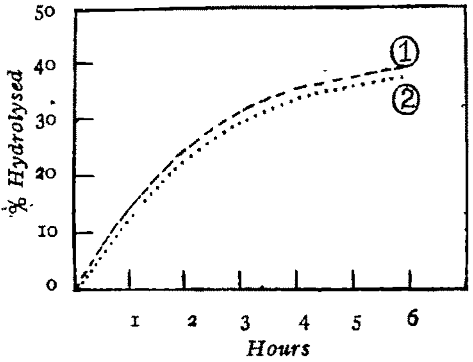


FIG. 3

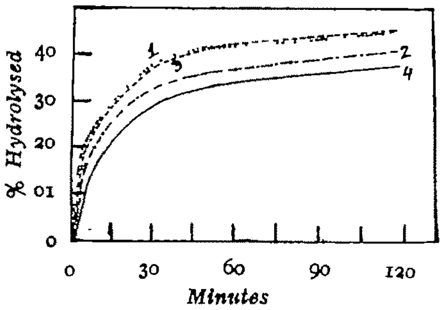


FIG. 4

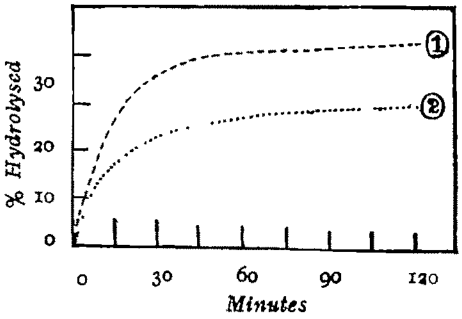
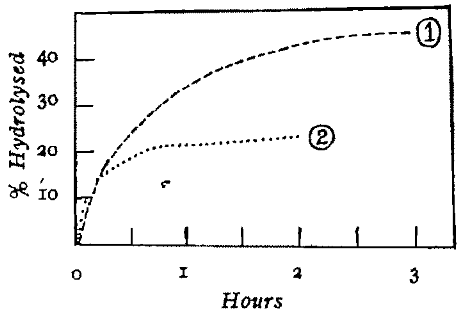


FIG. 5



was expected from the absorption curve. Still, however, it may be quite clear that they tend to maintain similar character and structure in all essential points. The peculiar behaviour of xylylamide can be attributed to its structure.

Moreover, it is evident, from this investigation, that the *ortho*-substituted compound shows a slower rate of hydrolysis than that of the *para*-substituted compound. This fact is in execllent agreement with a general view that "*ortho*-substitution always reduces the velocity" (Reid, *Amer. Chem. J.*, 1899, **21**, 284; Acree and Nirdlinger, *ibid* 1907, **38**, 489.). Mme. Ramart, Naik and Trivedi while studying hydrolysis of substituted amides of malonic acid found that *ortho*-derivative has got the lowest velocity of hydrolysis. This has been further substantiated by the other workers in this laborator[illegible]vedi, and Mehta, *J. Indian Chem. Soc.*, 1938, **15**, 426; Parikh, thesis for M.Sc., Bo[illegible]sity).

In Fig. 2 the velocities of hydr[illegible]acetoacet-α-naphthylamide and (2) acetoacet-β-naphthylamide are shown graphicall[illegible] seen that the greater absorption in the ultraviolet, exhibited by α-naphthylamid[illegible]d by the greater activity, as expressed by velocity of hydrolysis of the same. [illegible] the slight enhancement in the velocity of hydrolysis, when compared with the [illegible]ylamide, could be ascribed to the increased weight of grouping attached to the hyd[illegible]o group.

In support of the above suggest[illegible] urged that the molecular weights as well as the molecular volumes play an im[illegible] in determining the velocty of reaction as evidenced by the work of Kellas (*Z.* [illegible]*Chem.*, 1897, **24**, 221) in connection with the velocity of esterification. This fact h[illegible]n substantiated by the results of other investigators.

*Velocity of Hydrolysis in Acid Me*[illegible]—As regards the mechanism of the acid hydrolysis, different views are being held, though according to Rice (*loc. cit.*) the mechanism is similar to that which takes place in alkaline hydrolysis.

As stated before, in each exprriment a weighed quantity of 0.01 g.-mol. of the substance was dissolved in 100 c.c. of alcohol so as to make the ultimate concentration of the solution 0·1 g.-mol. per litre. 5 C.c. of this solution and 5 c.c. of 2·5 *N*-hydrochloric acid solution were introduced in each of the eight dry, clean, wide mouthed glass-stoppered bottles and these were at once placed in an electrically regulated thermostat, maintained at 35° at a known time. At each interval of 5,10,20,30 and 120 minutes, one bottle was removed from the thermostat, and ice-cold water (50 c.c.) was immediately added to arrest the reaction. 5 C.c of 0·1 *N*-sodium nitrite solution were then added and the bottle was kept in an ice-bath for 15 minutes so as to complete the diazotisation of the amine liberated during the course of hydrolysis. The excess of sodium nitrite was subsequently titrated with 0.05 *N*-sulphanilic acid solution, using starch-iodide paper. The end-point was marked when a drop of the titrated mixture failed to give the slightest blue colour. This method was adopted in accordance with the method suggested for the quantitative determination of an amine by Phillips and Lowry (*Ind. Eng. Chem. Anal. Ed.*, 1937, **29**, 381). In order to eliminate the discrepancy that may arise due to a loss of the nitrous acid by volatilisation, a blank experiment was carried out in each case, 5 c.c. of the solution of the substance being replaced by 5 c.c. of alcohol, but all along adhering to the identical procedure as described above.

The results of the study of the hydrolysis have been represented graphically in Fig. 3 and the summary of the results has been given in Table II.

### TABLE II

| Time in minutes. | Percentage hydrolysed of | | | | | | |
|---|---|---|---|---|---|---|---|
| | Acetoacet-anilide. | Acetoacet-*o*-tolylamide. | Acetoacet-*p*-tolylamide. | Acetoacet-1:3 4-xylylamide. | Acetoacet-α-naphthyl-amide. | Acetoacet-β-naphthyl amide. | Aceta-nilide. |
| 5 | 20·25 | 15·00 | 17·50 | 10·00 | 12·50 | 9·50 | 16·00 |
| 10 | 26·75 | 22·30 | 27·00 | 18·25 | 21·30 | 16·25 | 27 00 |
| 20 | 31·50 | 29·50 | 32·00 | 24·50 | 30·50 | 19·50 | 39·00 |
| 30 | 38·50 | 32·50 | 37·20 | 29·00 | 36·75 | 22·25 | 47·00 |
| 50 | 41·00 | 36·80 | 42·00 | 33·25 | 40·25 | 26·50 | 68·50 |
| 120 | 44·25 | 39·75 | 44·00 | 36·75 | 42·25 | 29·00 | 85·00 |

In Fig. 3 are given the curves showing the velocity of hydrolysis of (1) acetoacetanilide, 2) acetoacet-*o*-tolylamide, (3) acetoacet-*p*-tolylamide and (4) acetoacet-1:3:4-xylylamide.

It is clear from these curves that the velocity curves resemble the absorption ones in their general direction and disposition. Still, however, the similarity between these velocity curves and absorption curves, in this case, is not so much so close as it is observed in that of the results of alkaline hydrolysis. It can be assumed that the internal conditions of the molecules as regards he structure during alkaline hydrolysis remains the same as when they are studied for the ultraviolet absorption.

It is very interesting to note that the group-effect on the rate of hydrolysis is brought out here more conspicuously, because H-ion (catalyst) concentration remains the same. Any peculiar behaviour exhibited by the substances can be ascribed to the presence and arrangement of groups in the molecules.

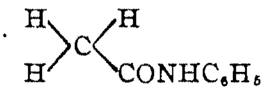
It is observed from the curves (2) and (3) that the proximity of the methyl group brings a remarkable diminution in the rate of hydrolysis in the *ortho*-compound. This point has already been noted during the study of alkaline hydrolysis. Reid (*loc. cit.*) during his studies on hydrolysis of acid amides, observed that substitution in the ring diminishes the rate of hydroysis by hydrogen ions, *ortho*-substitution having the greatest effect.

On comparing the curves (2) and (4) it appears that the effect of the methyl group in *ortho* position, present in acetoacet-1:3:4-xylylamide, becomes predominantly marked.

In Fig. 4 are shown the curves for the hydrolysis of (1) acetoacet-α-naphthylamide and (2) acetoacet-β-naphthylamide. On comparing these curves with those obtained in the case of alkaline hydrolysis, similar observations can be made.

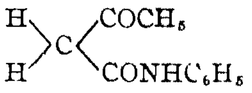
In Fig. 5 are plotted the curves for the acid hydrolysis of (1) acetoacetanilide and (2) acetanilide. From a study of these it is apparent that the introduction of $CH_3CO$ group in place of one of the hydrogens of the methyl group, situated in the side-chain of the molecule of acetanilide, considerably lowers the rate of hydrolysis.

If the structures of these substances are represented as below, it would be clearly observed that in case of acetanilide, the heavy residue, $-CONHC_6H_5$ is hanging on one of the valency bonds of carbon, the remaining three being utilised by single hydrogen atoms and so it s not balanced by any other group such as $CH_3CO-$. in acetoacetanilide.



$$\begin{matrix}H & & H\\ & C & \\ H & & CONHC_6H_5\end{matrix}$$

(Acetanilide)



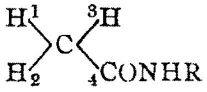
$$\begin{matrix}H & & COCH_5\\ & C & \\ H & & CONHC_6H_5\end{matrix}$$

(Acetoacetanilide)

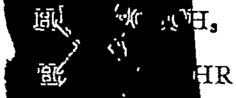
Eventually it may be expected that unequal distribution of valency pulls, which is highly increased in the case of acetanilide, is very likely responsible for the high chemical activity (*loc. cit.*).

Again, if we study the results of velocity of saponification of the substituted amides of cyanoacetic acid such as, $CH_2(CN)\cdot CONHR$, we notice that the unsymmetry in the molecule round the methylene group is responsible for the enhanced velocity of saponification of the groups -CONHR- (where R may be phenyl, tolyl, xylyl or naphthyl). However, if in the molecule there is a symmetry around the methylene group, the velocity of saponification is considerably lowered down, as exhibited by the study of the substituted amides of malonic acid, *viz.*, $CH_2$ $(CONHR)_2$ (Mme. Ramart, Naik and Trivedi, *loc. cit.*).

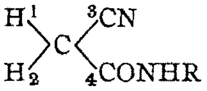
In a series such as,



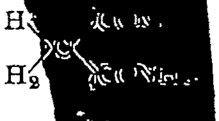
(I)



(II)



(III)



(IV)

the velocity of saponification is highest in the case of (I) and lowest in the case of (IV) as can be seen from the following :—

| Time. | Name. | % Hydrolysed |
|---|---|---|
| 3 hrs. | Acetanilide | 85% |
| " " | Acetone anilide | 26·16% |
| " " | Cyanoacetanilide | 24 00% |
| " " | M[illegible]anilide | 18·00% |

Two facts emerge out clearly from these observations.

1. Velocity of hydrolysis depends upon symmetry in the molecule.

2. The nature of groups such as -H, -CN, -CH$_3$, or -CONHR carried by the valency bond of carbon marked 3 plays an important part in deciding the speed of hydrolysis of the -CO·NHR attached to the bond marked 4.

From the above investigation, the following observations may be recorded.

1. The velocity of hydrolysis, (especially in alkaline medium) of the several compounds investigated, is in full accord with their absorption spectra.

2. The velocity of hydrolysis (alkaline or acid) appears to depend upon the nature of the radicals attached to the hydrolysable imino (-NH-) grouping.

3. The velocity of hydrolysis seems also to depend upon the position of the methyl group with regard to the imino group.

4. By introducing unsymmetry in a system like $\frac{X}{X}\!>\!C\!<\!\frac{Y}{Y}$ the relative rate of hydrolysis increases.

5. The molecular weight of the radicals attached to the imino group has also some influence on the rate of hydrolysis.

These are in excellent agreement with the observations recorded by previous workers.

The authors are greateful to H. H. The Maharaja Gaekwad's Government for necessary facilities given for carrying out the above work.

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# RELATIONS BETWEEN CHEMICAL ACTIVITY AND ABSORPTION IN THE ULTRAVIOLET OF CERTAIN ORGANIC MOLECULES. PART XI. VELOCITY OF REPLACEMENT OF THE CHLORINE ATOMS IN THE CHLORO DERIVATIVES OF THE SUBSTITUTED AMIDES OF ACETOACETIC ACID

By R. K. Trivedi and B. N. Mankad

Chemical activity of the substances mentioned below as expressed by the velocity of replacement of the chlorine atom has been correlated with their absorption spectra: (1) monochloroacetoacetanilide, (2) monochloroacetoacet-1:3:4-xylylamide, (3) monochloroacetoacet-α-naphthylamide.

Results indicate that the following factors influence the velocity of replacement of the chlorine atom by hydrogen: (*i*) the position as well as the spatial arrangement of the radicals like the methyl groups in the nuclear rings attached to the carbonyl groups of these groups; (*ii*) the unsymmetry of the group round the central carbon, resulting into unbalanced unilateral tension The replacement of chlorine increases in rapidity as we pass from monochloroacetoacetanilide, through monochloroaceto-1:3:4-xylylamide to monochloroacetoacet-α-naphthylamide, it being the most rapid in the last case.

These investigations have been undertaken with a view to see if the velocity of replacement of chlorine in compounds such as (1) monochloroacetoacetanilide, (2) monochloroacetoacet-1:3:4-xylylamide and (3) monochloroacetoacet-α-naphthylamide, is correlated with the nature and position of the groups attached to the carbonyl radicals having -CHCl- complex in between. It is possible that the activity of the chlorine atom, thus situated in the molecule, may be influenced by the same factors which govern the lability of the hydrogen atoms of the methylene group ($-CH_2-$) situated between two carbonyl groups in the case of the amide derivatives of acetoacetic acid; and this phase of the activity of molecules may be correlated with their absorption in the ultraviolet.

The velocity of replacement of chlorine atom has been studied on the basis of the reduction of chlorine atom in the molecule by means of hydrogen iodide. This is brought about by treating the chloro compound by means of hydriodic acid generated by the action of hydrochloric acid and potassium iodide (Kurt and Meyer, *J. Chem. Soc.*, 1921, **119**, 951, 305).

The method used for the determination of the velocity of replacement of the chlorine atom by hydrogen, can be outlined as follows.

The substance (0·001 g.-mol.) was dissolved in 98% alcohol and the volume was made up to 100 c.c. so as to have an ultimate concentration of 0·01 g.-mol. per litre. In a wide-mouthed glass-stoppered bottle 5 c.c. of the above solution were run in with the help of a burette. Consecutively 5 c.c. of 0·5 *N*-HCl and 0·5 *N*-KI solution were also run in the same bottle. Eight such bottles were placed simultaneously at a known time in electrically regulated thermostat, maintained at 35°. At suitable intervals of 1, 3, 5, 10, 25, 45, 70 and 100 minutes, one bottle at a time was removed from the thermostat and 50 c.c. of ice-cold water were added to the reacting mixture in order to arrest the reaction. The iodine liberated during the reaction, was then titrated immediately with 0·01*N*-sodium thiosulphate using 1 c.c. of 1% starch-solution.

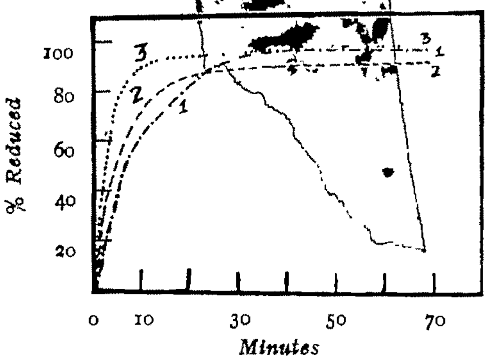
Simultaneously with the above set of experiments, an equal number of bottles containing the reacting mixture without the chloro compound was placed in the thermostat for a blank check.

The results obtained are summari[illegible]

| Time interval in minutes. | [illegible] reduced of<br>Monochloroaceto[illegible] anilide. | [illegible]loro acetoacet-[illegible]4-xylyamide. | Monochloroacetoacet-α-naphthylamide. |
|---|---|---|---|
| 1 | 7·25 | 22·50 | 24·50 |
| 3 | 25·25 | 36·50 | 55·00 |
| 5 | 40·00 | 55·00 | 77 65 |
| 10 | 60·00 | 73·00 | 89 75 |
| 25 | 90·75 | [illegible]8·75 | 95·00 |
| 45 | 97·25 | [illegible]1·50 | 97·00 |
| 70 | 97·75 | 91·75 | 98·00 |
| 100 | 98·00 | 9[illegible]·00 | 99·00 |

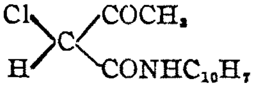
In Fig. 1 are drawn the curves for the velocity of reduction of the chlorine atom in the compounds (1) monochloroacetoacetanilide, (2) monochloroacetoacet-1:3:4-xylylamide and (3) monochloroacetoacet-α-naphthylamide.

FIG. 1.



It will be seen that the relative position and disposition of the velocity curves (1) and (2) are in good accord with those of the absorption curves of these substances.

Moreover, it appears that the percentage of the substance reduced in 100 minutes is higher in the case of monochloroacetoacet-α-naphthylamide. In the case of this compound,



$$\begin{array}{l} Cl \diagdown \qquad \diagup COCH_3 \\ \qquad C \\ H \diagup \qquad \diagdown CONHC_{10}H_7 \end{array}$$

the valency-bond represented by the arrow may appropriate a large amount of the total force of valency of the central carbon atom, with the consequence that a small amount of the valency force is left over to keep attached the chlorine atom and so it becomes readily reduced.

It will also be seen from the table and the curves plotted, that at the start, replacement of chlorine is peculiarly rapid and increases in rapidity as we pass from monochloroacetoacetanilide through monochloroacetoacet-1:3:4-xylylamide to monochloroacetoacet-α-naphthylamide, it being the most rapid in the case of the last one.

From these observations, it can be assumed that [illegible] peculiar behaviour may be attributed to the influence of the other groups attached to the carbon atom, to which also the chlorine atom is linked, as also to the influence of the methyl groups present in the nucleus.

Further, in this case, the behaviour exhibited by these substances, can be attributed to the following factors which are supposed to influence the velocity of replacement of the chlorine atom by hydrogen :—

1. The position of the radicals like the methyl groups, in the nuclear rings attached to the carbonyl groups, as well as the spatial arrangement of these groups.

2. The unsymmetry of the group round the central carbon, resulting into an unbalanced unilateral tension.

It will be interesting here to refer to the results of a similar work carried out in this laboratory, in connection with the replacement of the chlorine atom, in compounds such as, $ClHC\cdot(CONHR)_2$, $Cl_2C(CONHR)_2$ (Mehta, M.Sc. Thesis, 1939. Bomb. Univ.).

From reference to the results (obtained by Naik, Trivedi and Mehta, Part II, of this series, this Journal, 1943, **20**, 355), it will be seen that Pichloromalondi-1:3:4-xylylamide is not reduced at all. This has been explained on the basis that symmetry round the central carbon atom makes the whole molecule more stable with the consequence of non-reducibility of the chlorine atoms under experimental conditions. It is quite apparent from the results that as soon as the symmetry is disturbed, the reactivity of the molecule appears to be enhanced, as expressed by the velocity of reduction of the chlorine atom in the corresponding monochloromalon-di-1:3:4-xylylamide, which is in accordance with the results obtained by measuring the velocity of hydrolysis of this class of compounds.

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